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ABSTRACTS OF PAPERS

ON

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JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

PHYSICAL, INORGANIC, MINERALOGICAL, PHYSIOLOGICAL, AGRICULTURAL,

AND

ANALYTICAL CHEMISTRY.

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Substitution of Chlorine and Bromine in the Fatty Series.
By A. D. HERZFELDER (*Ber.*, **26**, 2432—2438).—The following is a
translation of the author's own summary of his results.

When into a monohalogen compound a second halogen atom is in-
troduced, it always attaches itself to that carbon atom which is
situated next to the carbon atom already united with halogen. In
the case of further substitution, this rule only holds for bromine, of
which it is never possible, by other than violent means, to attach
more than 1 atom to each atom of carbon. On the other hand, when
a third atom of chlorine is introduced, it frequently attaches itself to
a carbon atom that is already united with chlorine.

Bromides that already contain 1 atom of bromine united with each
atom of carbon, cannot easily be further brominated; chlorides, how-
ever, take up more chlorine. A normal hydrocarbon, when brominated
by ordinary means, takes up as many atoms of bromine as it contains
atoms of carbon; this was shown in the case of methane, ethane,
propane, and also, although not with absolute certainty, in that of
butane, hexane, heptane, and octane.

The chloropropanes yielded the following compounds on further
chlorination.

$CH_3 \cdot CH_2 \cdot CHCl_2$ gives $CH_3 \cdot CHCl \cdot CHCl_2$.
$CH_2Cl \cdot CH_2 \cdot CH_2Cl$ „ $CH_2Cl \cdot CH_2 \cdot CHCl_2$.
$CH_3 \cdot CHCl \cdot CH_2Cl$ „ $CH_3 \cdot CHCl \cdot CHCl_2$.

$$CH_3 \cdot CCl_2 \cdot CH_3 \quad \text{gives} \quad CH_3 \cdot CCl_2 \cdot CH_2Cl.$$
$$CH_2Cl \cdot CHCl \cdot CH_2Cl \quad ,, \quad CH_2Cl \cdot CHCl \cdot CHCl_2.$$
$$CH_3 \cdot CCl_2 \cdot CH_2Cl \quad ,, \quad CH_2Cl \cdot CCl_2 \cdot CH_2Cl$$
$$CH_3 \cdot CHCl \cdot CHCl_2 \quad ,, \quad \text{Pentachloropropane.}$$
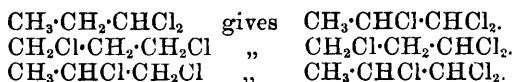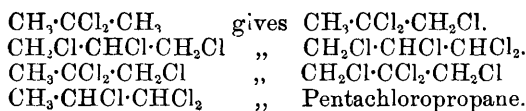
C. F. B.

Formation of Ethereal Salts by Double Decomposition. By
G. BERTONI (*Chem. Centr.*, 1893, ii, 362—363; from *Arch. sci. phys.
nat. Genève*, **15**, 1—23).—Ethereal salts may be obtained by double
decomposition in a similar way to inorganic salts ; and when one of
the products of the reaction is removed from the sphere of action
as it is formed, the action is complete.

If methylic alcohol is gradually added to pure glycerylic nitrite at
the ordinary temperature, a brisk reaction sets in, and 97 per cent. of
the theoretical yield of methylic nitrite distils over. The reaction is
somewhat less complete with ethylic alcohol, and still less so with
isopropylic, isobutylic, and amylic alcohols.

The same double decomposition may be brought about in a sealed
tube, provided that the final products will separate into two layers.
When the nitrite of ethylene glycol is prepared in this way by mixing
glycerylic nitrite and glycol, a homogeneous opalescent liquid is
obtained which separates into two layers when heated or when mixed
with dry ether.

A comparison of the boiling points of the alcohols and their
nitrites shows a very simple relation.

	Amylic.	Iso-butylic.	Iso-propylic.	Ethylic.	Methylic.
B. p. of alcohol..	132°	107°	84°	78°	67°
B. p. of nitrite ..	92	67	44	18	−13

The difference in the boiling points is 40°, or $40° + \frac{40}{2}°$ for ethylic
alcohol and $2 \times 40°$ for methylic alcohol.

The author has prepared the following ethereal salts by this
method. *Allylic nitrite* is a limpid, yellowish liquid which has the
sp. gr. 0 9546, and boils at 43·5—44 5°. The boiling point of allylic
alcohol is 96°, and the boiling point of the nitrite is $96° - (40° + \frac{40}{2}°)$
$= 46°$. *Ethylenic nitrite* is a limpid, yellowish liquid which has a
very unpleasant odour, is poisonous, and boils at 96—98° ; the sp. gr.
$= 1 2156$. The boiling point calculated from the boiling point of
the glycol (197°) by the formula $197° - (2° \times 40° + \frac{40}{2}°) = 97°$.
The *tertiary butylic nitrite* is a limpid, pale yellow liquid which has
an unpleasant odour, and boils at 62·8—63 2° ; the sp. gr. $= 0·8914$.
The boiling point is calculated from the equation $83° - \frac{40}{2}° = 63°$.

E. C. R.

Preparation and Properties of Potassium Cyanate. By H.
ERDMANN (*Ber.*, **26**, 2438—2443).—Potassium cyanate may be con-
veniently prepared in the following manner; it is not advantageous
to use larger quantities in one operation than those given. 200 grams
of completely dehydrated potassium ferrocyanide, while still warm, is
triturated with 150 grams of fused potassium dichromate, and the
mixture heated in a large nickel or iron dish. The black product is

powdered, and boiled on the water bath, with frequent shaking, for 10 minutes with a mixture of 900 c.c. of 80 per cent. alcohol and 100 c.c. of methylic alcohol. The clear solution is then decanted through a folded filter into a large beaker standing in ice and water; the vessel containing the black residue is also placed in ice and water to prevent decomposition. Potassium cyanate separates out in the beaker, and is drained on a filter with the pump; the mother liquor is used again to extract the black residue, as above, the process being repeated three or four times. The accumulated cyanate (about 65 grams) is then washed with ether and dried in a vacuum over sulphuric acid; it is nearly pure, containing only a trace of carbonate. The alcoholic mother liquor cannot be worked up for cyanate by boiling it down, for the cyanate then completely decomposes into carbonate and ammonia; carbamide may, however, be obtained from it by adding ammonium sulphate (70 grams), evaporating to dryness, and extracting the residue with 96 per cent. alcohol. C. F. B.

Antimony-blue. By G. SEBOR (*Chem. Centr.*, 1893, ii, 318—319; from *Casopis proprumsyl chemicky*, **3**, 216).—Antimony-blue is prepared by dissolving antimony sulphide in concentrated hydrochloric acid, and, after filtering, adding to the boiling liquid a concentrated solution of potassium ferrocyanide and some potassium chlorate or nitric acid; the precipitate is dried at $100°$. An antimony-blue is also obtained by mixing antimony chloride and potassium ferrocyanide, and adding a large quantity of water. When prepared in this way, it contains some basic antimony chloride. A sample of pure antimony-blue gave, on analysis, $Fe = 30·28$, $Sb = 2·422$, $H_2O = 5·828$, $Cl = 0·712$, $O = 0·323$, and $CN = 60·435$ per cent. The blue is insoluble in cold hydrochloric, sulphuric, and nitric acids: when boiled with hydrochloric or sulphuric acid, it yields hydrocyanic acid. Dilute sodium and potassium hydroxides and ammonia only attack it when warmed. When heated with nitric acid, it is converted into a greyish-green compound. Unlike Prussian-blue, it is not soluble in a solution of an oxalate or tartrate. E. C. R.

Glucosides of the Alcohols. By E. FISCHER (*Ber.*, **26**, 2400—2412).—A number of sugars have been found to form condensation products of the nature of glucosides, with alcohols and hydroxy-acids. These compounds do not react with alkalis, with Fehling's solution, or with phenylhydrazine, but they are decomposed, although more slowly than cane sugar, by boiling with dilute acids, or by the action of invertase or active yeast, into the original alcohol and sugar. That they do not react with phenylhydrazine shows that they no longer contain a carbonyl group; this group in the original sugar must therefore have taken part in the condensation. As for the hydroxyl, which must also have contributed to the water formed in the reaction, it cannot have been that united with the α carbon atom, for the product obtained (this vol., i. 38) by condensing an alcohol with benzoin (which contains a $CH·OH$ group in the α-position to a CO group), does react with phenylhydrazine. It is most probable that the γ-hydroxyl group is the one concerned, and, in this case, the

product formed from methylic alcohol and glucose with loss of water will have the formula

$$OH \cdot CH_2 \cdot CH(OH) \cdot CH < \frac{CH(OH) \cdot CH(OH)}{O} > CH \cdot OMe.$$
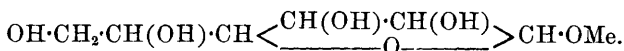
These compounds are named by combining the name of the alcohol with that of the sugar; thus, ethylrhamnoside denotes the condensation product formed from ethylic alcohol and rhamnose. They are prepared by dissolving the sugar in the alcohol, and saturating the solution in the cold with gaseous hydrogen chloride; when the sugar is insoluble in the alcohol, it is dissolved in a little water, and the solution mixed with excess of a saturated alcoholic solution of hydrogen chloride, or an acetyl derivative of the sugar may be dissolved in the alcohol, and the solution saturated with hydrogen chloride, in which case the same product is obtained as when the sugar itself is used. For details of the process by which the product is purified and obtained crystallised, reference must be made to the original paper. Most of these substances are sweet, but benzylglucoside and ethylrhamnoside are bitter.

Methylglucoside, $C_6H_{11}MeO_6$, forms colourless crystals, melts at 165—166° (uncorr.), and has specific rotation $[\alpha]_D^{20°} = +157\cdot5°$. *Methylarabinoside,* $C_5H_9MeO_5$, crystallises in colourless needles or plates, and melts at 169—171° (uncorr.). *Ethylarabinoside,* $C_5H_9EtO_5$, forms stellate groups of crystals, and melts at 132—135° (uncorr.). *Ethylrhamnoside* is a colourless, bitter syrup; so is *methylrhamnoside.* *Ethylglucoside* was obtained as a partly crystalline, partly amorphous, mass, and is identical with the "diglucose" of Gautier (*Bull. Soc. Chim.,* [2], **22,** 145). *Benzylglucoside* was also obtained as a bitter, partly crystalline, partly amorphous, mass. *Glycolglucoside* forms a colourless syrup. *Lactic acid glucoside* was obtained as a hygroscopic, white powder.   C. F. B.

Quinovose and "Quinovite." By E. FISCHER and C. LIEBERMANN (*Ber.,* **26,** 2415—2420).—"Quinovite" is shown to be really *ethylquinovose,* $C_6H_{11}EtO_5$, for it is converted by boiling with dilute acids into ethylic alcohol and a sugar, to which the name *quinovose* is given. Quinovose is shown, by analysis of its osazone, to have the composition $C_6H_{12}O_5$; further, it yields 2 : 5-methylfurfuraldehyde when distilled with dilute hydrochloric acid, and so must be a methylpentose, $OH \cdot CHMe \cdot [CH \cdot OH]_3 \cdot CHO$. From this follows the formula given above for "quinovite," which agrees well with the analyses of the substance, and of its triacetyl derivative published by Liebermann and Giesel (*Ber.,* **16,** 935 ; Abstr., 1884, 1191).

Quinovose was obtained as a yellowish syrup with a sweet, at the same time slightly bitter, taste; it is oxidised by bromine water to an acid, readily reduces Fehling's solution, and with phenylhydrazine yields *phenylquinovosazone,* $C_6H_{10}O_3(N_2HPh)_2$, which crystallises in minute, yellow needles, and melts at 193—194° (uncorr.).

     C. F. B.

Action of Lime and Alkalis on Invert Sugar. By L. JESSER (*Chem. Centr.,* 1893, ii, 364—365; from *New. Zeit. Rüb.-Zucker-Ind.*

31, 3—11).—A 0·2--0·4 per cent. solution of glucose was treated with different quantities of lime, and the product, after precipitating the lime with carbonic acid, was examined, and the lime and dry substance determined in it. With moderate proportions of lime, and at temperatures below the boiling point, 100 grams of glucose gave 109·8 grams of dry substance containing 16·85 parts of calcium (? oxide) and 92·95 parts of organic matter. With a more intense action of the lime, 102·4 grams of dry substance was obtained, containing 16·7 parts of calcium (? oxide) and 85·7 parts of organic constituents. This product is not altered by prolonged boiling with caustic lime. A solution of lævulose, treated in the same way, is at 80° already converted into products which are unaltered by boiling with lime, that is, the lime acts more readily on lævulose than on glucose. From the above results, it is possible to calculate the quantity and composition of the product formed by the action of lime on invert sugar; and the author obtained by experiment numbers which agreed with those calculated. The products are neutral calcium salts which are not optically active. do not reduce Fehling's solution, and, when treated with sulphuric acid, yield volatile acids.

When a mixture of alkali and lime is employed in the place of lime alone, similar products are obtained containing the alkali in place of lime.

The ratio of the lime combined with these acids to that of the glucose employed is $1\frac{1}{2}$ mol. of calcium (? oxide) to 2 mols. of glucose, and this ratio is not altered by boiling with excess of alkali.

E. C. R.

Resolution of Starch by the Action of Diastase. By C. J. Lintner and G. Düll (*Ber.*, **26**, 2533—2547).—By the action of phenylhydrazine on beer extract, isomaltosazone is formed, but at present it is uncertain whether the compound is identical with that of E. Fischer, and of Scheibler and Mittelmeier. The authors criticise the theory of Brown and Morris on the resolution of the starch molecule (Trans., 1889, 449), and suggest that the various amyloïns are merely mixtures of dextrin and isomaltose. Five definite compounds are formed by the action of diastase on starch, namely, isomaltose and maltose, and three dextrins, for which the names amylodextrin, erythrodextrin, and achroodextrin are suggested. These substances were isolated by treating the solutions with alcohol of various strengths; their purity was determined by means of the refractive power, molecular weight by Raoult's method, and their behaviour towards phenylhydrazine, alkaline copper solution, and iodine in the manner fully described in the original paper.

Amylodextrin, $(C_{12}H_{20}O_{10})_{54}$, the first decomposition product of starch, is a fine, white powder; it is sparingly soluble in cold water, but dissolves on heating in almost every proportion, and readily forms supersaturated solutions; spheroïdal crystals are readily deposited from solutions containing 20—30 per cent. The refractive power $[\alpha]_D = 196°$. The compound gives a deep blue coloration with iodine, and does not reduce alkaline copper solution. Amylodextrin is the chief constituent of " amidulin," " soluble starch," &c.

Erythrodextrin, $(C_{12}H_{20}O_{10})_{18} + H_2O = (C_{12}H_{20}O_{10})_{17}\cdot C_{12}H_{22}O_{11}$, is

formed by the action of diastase on the preceding compound, and is
deposited from dilute alcoholic solution in spheroïdal crystals. It
reduces alkaline copper solution, and gives a reddish-brown coloration
with iodine. The refractive power $[\alpha]_D = 196°$.

Achroodextrin, $(C_{12}H_{20}O_{10})_6 + H_2O = (C_{12}H_{20}O_{10})_5 \cdot C_{12}H_{22}O_{11}$, is extremely soluble in water; in alcoholic solution crystals are formed
which could not be isolated. It readily reduces alkaline copper solution, gives no coloration with iodine, and has a slight sweet taste.
The refractive power $[\alpha]_D = 192°$.

Isomaltose, $C_{12}H_{22}O_{11}$, has not yet been obtained in crystals; it
undergoes fermentation in presence of yeast, is converted into maltose
by the action of diastase, and readily reduces copper solution. The
refractive power $[\alpha]_D = 140°$. The osazone (see above) melts at
150—153°. The successive stages in the decomposition of amyl•
dextrin by the action of diastase are represented by the following
equations.

$$(C_{12}H_{20}O_{11})_{54} + 3H_2O = 3[(C_{12}H_{20}O_{10})_{17}.C_{12}H_{22}O_{11}].$$
<div align="center">Erythrodextrin.</div>

$$3[(C_{12}H_{20}O_{10})_{17},C_{12}H_{22}O_{11}] + 6H_2O = 9[(C_{12}H_{20}O_{10})_5,C_{12}H_{22}O_{11}].$$
<div align="center">Achroodextrin.</div>

$$9[(C_{12}H_{20}O_{10})_5,C_{12}H_{22}O_{11}] + 45H_2O = 54C_{12}H_{22}O_{11} = 54C_{12}H_{22}O_{11}.$$
<div align="center">Isomaltose.   Maltose.</div>
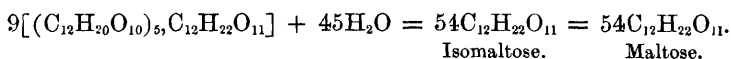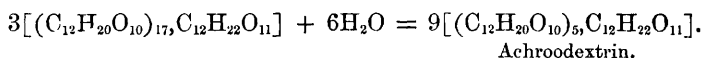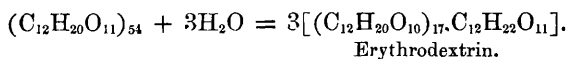
The authors point out that in ordinary circumstances all these
changes occur simultaneously.   J. B. T.

Soluble Gums. By P. PALLADINO (*Bull. Soc. Chim.*, [3], **9,**
578—580).—Soluble gums never contain starch. The presence of
dextrin is difficult to recognise, but if an alkaline solution of a gum
is boiled for a minute with aniline sulphate, chlorobrucine, pure
brucine, orcinol, or orceïn, the liquid remains pale yellow with a
greenish tinge, in the absence of dextrin, but becomes orange-yellow
or brownish-red if the latter is present. Other results are given
in the following table. (1) is the sp. gr. at 15° of solutions con-

	1.	2.	3.	4.
Kordofan.	1·0450	1·4166	6·29	−26·47
Galam	1·0448	1·3333	7·23	+ 2·11
Salabreda	1·0448	1·4166	8·18	+14·57
Bas du Fleuve	1·0450	1·5000	6·92	−28·47
Arabic (Kordofan)	1·0454	1·3333	6·92	−23·02
Zula	1·0448	1·1666	7·23	+12·84
Gheziri	1·0446	1·3333	9·75	+45·01
Amrad	1·0425	1·3333	5·03	+71·81
Australia	1·0438	1·1666	5·03	+62·21
Cape	1 0395	1·5000	7·86	+33·09
Suakim	1·0450	1·3333	10·06	−21·17
Turique.	1·0450	1·5833	9·12	+34·41
Geddah	1·0449	1·4166	5·34	−24·87

taining 13 024 grams of the gum in 100 c.c.; (2) is the viscosity of the same solution as compared with water; (3) is the acidity in terms of arabic acid; (4) is the specific rotation, $[a]_D$, at 16°.

The rotatory powers of solutions of different parts of the same frag‧ment of gum are different. There is no constant relation between the rotatory power of the gum solution and the quantity of gummic acid obtainable from it; neither is there any relation between the rotatory power of the gum and that of the sugars obtained from it by the action of acids. C. H. B.

Dimethylbutylamine. By P. Eschert and M. Freund (*Ber.*, **26**, 2490—2493; compare Abstr., 1891, 1172).—Dimethylbutylamine, $CMe_2Et \cdot CH_2 \cdot NH_2$, is prepared by the reduction of ethyldimethylacetonitrile; it boils at 113—114°, and readily absorbs water and carbonic anhydride; the *hydrochloride*, $C_6H_{15}N,HCl$, crystallises from a mixture of alcohol and ether, and melts at 225—228°. The *platinochloride*, $(C_6H_{15}N)_2,H_2PtCl_6$, crystallises from water, and decomposes at about 210°. The *aurochloride*, $C_6H_{15}N,HAuCl_4$, crystallises in needles. The *phenylthiocarbamide*, $NHPh \cdot CS \cdot NH \cdot CH_2 \cdot CMe_2Et$, is deposited from alcohol in needles melting at 120—121°. The *phenylcarbamide*, $NHPh \cdot CO \cdot NH \cdot CH_2 \cdot CMe_2Et$, melts at 103—105°. *Dihexyloxamide*, $C_2O_2(NH \cdot CH_2 \cdot CMe_2Et)_2$, crystallises from alcohol in needles, and melts at 102°. By the action of silver nitrite on the hydrochloride, an alcohol is obtained which boils at 119—122°; it has the formula $C_6H_{14}O$, but the quantity obtained was too small to determine whether it was methyldiethylcarbinol (b. p. 121—122·5°), or dimethylpropylcarbinol (b. p. 122·5—123·5°); the authors suggest that it is the former compound. Allylamine hydrochloride, when treated with silver nitrite, yields allylic alcohol, but no acetone. J. B. T.

Guanidine Derivatives of Bibasic Acids. By W. Traube (*Ber.*, **26**, 2551—2558).—Guanidine reacts with ethylic oxalate and ethylic malonate to form derivatives which correspond in composition and chemical properties with parabanic acid and barbituric acid, the urea residue of these being replaced by the guanidine residue. *Oxalylguanidine*, $HN:C\underset{NH \cdot CO}{\overset{NH \cdot CO}{<}|}$, is precipitated by acetic acid from its solution in ammonia, in the form of white crystals containing $1H_2O$, which is lost at 160°. The anhydrous compound is insoluble in alcohol and ether, slightly soluble in water. It readily dissolves in alkalis, but decomposes into oxalic acid and guanidine when the solutions are allowed to remain in the cold, or more rapidly on boiling. It dissolves in concentrated mineral acids, and may be recrystallised from hot dilute hydrochloric acid. When heated, it decomposes without melting.

Malonylguanidine, $CH_2\underset{CO \cdot NH}{\overset{CO \cdot NH}{<}}>C:NH$, also crystallises with $1H_2O$, which is lost at 110°. It is slightly soluble in hot water, almost insoluble in cold water and alcohol, and dissolves in alkalis, alkali carbonates, ammonia, and concentrated acids. When boiled

with alkalis, it is decomposed into guanidine and malonic acid. It behaves as a monobasic acid, and forms a *barium salt*, $(C_4H_4N_3O_2)_2Ba +$ $8H_2O$, which is only slightly soluble in cold water. The *calcium salt* is readily soluble in hot, slightly in cold, water. *Dibromomalonylguanidine*, $C_4H_3Br_2N_3O_2$, is prepared by the direct action of bromine on malonylguanidine. It forms slender, almost colourless needles, and when heated decomposes with evolution of bromine vapour without previously melting. It is insoluble in alcohol and ether, slightly soluble in hot water, and dissolves readily in alkalis. It is not altered by boiling with water, but is decomposed by boiling aqueous alkalis. *Nitromalonylguanidine*, $HN:C:(NH:CO)_2:CH\cdot NO_2$, obtained by the action of fuming nitric acid on malonylguanidine, is a faintly yellowish, crystalline powder, which deflagrates when gently heated. Like dilituric acid, the corresponding urea derivative, it dissolves in alkalis with an intense yellow colour. The *ammonium*, *sodium*, and *calcium salts* are yellow, crystalline substances, only slightly soluble in cold water.

Isonitrosomalonylguanidine, $HN:C:(NH\cdot CO)_2:C:NOH$, is formed by the action of nitrous acid on malonylguanidine. The *ammonium salt*, which forms lustrous, violet blue crystals containing $1H_2O$, decomposes on heating, some ammonia being evolved along with the water. It is very slightly soluble in cold, more readily in hot, water. Aqueous potash converts it into the *potassium salt*, which forms dark rose-red plates. The *sodium salt* is dark violet, and forms a purple solution in water. The *calcium salt*, with $4H_2O$, forms very slender, light red needles. The free isonitrosomalonylguanidine is separated from its salts, on treatment with dilute sulphuric acid, as a greyish green, slimy mass, which is insoluble in water, and becomes red when boiled with water or exposed to the air. It dissolves in concentrated acids, and is oxidised by nitric acid to the nitro-compound.

Amidomalonylguanidine, $HN:C:(NH\cdot CO)_2:CH\cdot NH_2$, is obtained by the action of hydrogen sulphide on a solution of isonitrosomalonylguanidine in hydrochloric acid. When the ammonium salt of the isonitroso-compound is boiled with a solution of ammonium hydrogen sulphite, a colourless solution is formed, from which crystals separate on cooling; these have the composition

$$HN:C:(NH\cdot CO)_2:CH\cdot NH\cdot SO_3\cdot NH_4,$$
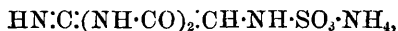
and correspond with the ammonium salt of thionuric acid in the urea derivatives. On treatment with dilute acids, this substance decomposes with formation of sulphuric acid and amidomalonylguanidine, the sulphate of which crystallises out on cooling. Amidomalonylguanidine is a yellowish powder which is scarcely soluble in water, and rapidly becomes dark red when exposed in a moist state to the air. It dissolves in acids, with which it forms crystalline salts, and is also soluble in alkalis. Both the base and its salts reduce ammoniacal silver solution, and are oxidised by the halogens or concentrated nitric acid with formation of oxalylguanidine. When an ammoniacal solution of the amido-base is oxidised by a current of air, or by

mercuric oxide, a solution is obtained resembling in colour a concentrated permanganate solution. The compound formed, which possibly corresponds with murexide, is very unstable, and could not be isolated.

Imidopseudouric acid, $HN:C:(NH\cdot CO)_2:CH\cdot NH\cdot CO\cdot NH_2$, is prepared by dissolving the amido-compound in a boiling concentrated solution of potassium cyanate. It crystallises with $1H_2O$, which is lost at 135°, and is readily soluble in hot water, from which it separates on cooling in lustrous, slightly yellowish needles. The yellow *silver salt* rapidly decomposes with separation of silver.

A. H.

Properties and Constitution of Hydroxylamine and its Homologues. By J. W. BRÜHL (*Ber.*, **26**, 2508—2520) —Hydroxylamine was prepared by Lobry de Bruyn's method by the action of sodium methoxide on hydroxylamine hydrochloride, and the product fractionated in a vacuum. The yield is 66 per cent. of the theoretical. The preparation of methylhydroxylamine and of ethylhydroxylamine has been recently described by Kjellin (next abstract); the instability of the latter compound probably accounts for the variations in its physical constants. The following results have been obtained. Hydroxylamine, sp. gr. $0°/4° = 1\cdot2255$; $23\cdot5°/4° = 1\cdot2044$. $\mathfrak{M}a = 7\cdot193$; $\mathfrak{M}_{Na} = 7\cdot228$; $\mathfrak{M}_\gamma - \mathfrak{M}a = 0\cdot190$. The refractive indices were determined at 23·5°. Methylhydroxylamine, sp. gr. $20°/4° = 1\cdot0003$; $\mathfrak{M}a = 11\cdot74$; $\mathfrak{M}_{Na} = 11\cdot80$; $\mathfrak{M}_\gamma - \mathfrak{M}a = 0\cdot31$. Ethylhydroxylamine, sp. gr. $63\cdot9°/4° = 0\cdot9079$; $\mathfrak{M}a = 16\cdot78$; $\mathfrak{M}_{Na} = 16\cdot83$; $\mathfrak{M}_\gamma - \mathfrak{M}a = 0\cdot39$.

In the course of some hitherto unpublished work, the author has determined the refractive powers of ethylamine and of methylamine. The results are: Methylamine, $\mathfrak{M}a = 10\cdot23$; $\mathfrak{M}_{Na} = 10\cdot25$; $\mathfrak{M}_\gamma - \mathfrak{M}a = 0\cdot29$. Ethylamine, $\mathfrak{M}a = 14\cdot80$; $\mathfrak{M}_{Na} = 14\cdot85$; $\mathfrak{M}_\gamma - \mathfrak{M}a = 0\cdot40$. With the help of these values, and knowing the refractive power of ammonia, and of CH_2, it is possible to calculate the separate values for oxygen and nitrogen. The mean values are: O, $r_a = 1\cdot535$; $r_{Na} = 1\cdot565$; $r_\gamma - r_a = 0\cdot015$. N·O, $r_a = 2\cdot332$; $r_{Na} = 2\cdot495$; $r_\gamma - r_a = 0\cdot072$.

The numbers derived from ethylhydroxylamine are omitted, for 'the reason stated above. The above refractive power of oxygen is practically identical with that deduced from observations of water and organic compounds containing hydroxyl; the ordinary formula for hydroxylamine is, therefore, confirmed on physical grounds.

J. B. T.

Substituted Hydroxylamines. By C. KJELLIN (*Ber.*, **26**, 2377—2385).—In order to obtain the β-substituted hydroxylamines, none of which have previously been isolated, the author prepared the corresponding nitrogen substituted derivative of metanitrobenzaldoxime (syn-) by the action of an alcoholic solution of sodium ethoxide and an alkyl iodide, and, by distillation with steam, separated this from the oxygen substituted ether formed at the same time, the latter being easily volatile; the compound was then decomposed by boiling it with concentrated hydrochloric acid.

β-Ethyhyldroxylamine, NHEt·OH, cannot be prepared from its hydrochloride by the action of potash, and the method employed by de Bruyn for the isolation of hydroxylamine (Abstr., 1892, 402) was therefore used. The hydrochloride of the base, which can only be obtained in the form of a brown oil, is dissolved in a small amount of methylic alcohol, and treated with rather less than the calculated amount of sodium methoxide; as the reaction is accompanied by considerable development of heat, the liquid must be cooled. The sodium chloride which separates is filtered off through an asbestos filter, paper being attacked by the base, and the filtrate distilled under a pressure of 15 mm. Methylic alcohol passes over first, followed by a solution of the base in the alcohol, and then the ethyl-hydroxylamine begins to sublime in groups of small crystals. This substance, after being pressed on a porous plate, forms colourless, odourless, crystalline plates with a pearly lustre, and melts without decomposition at 59—60°. The crystals are somewhat indistinct, and could not be measured. It is very readily soluble in water and methylic and ethylic alcohols, less readily in ether, benzene, and light petroleum, in the cold, but dissolves in the last named more readily on heating, and is deposited in long needles on cooling. It deliquesces in the air when exposed in loosely stoppered vessels, but when freely exposed volatilises without previous deliquescence; its vapour combines with hydrogen chloride to form white fumes of the hydrochloride. This base has a strongly alkaline reaction, attacks organic matter very vigorously, and reduces copper and silver salts as strongly as hydroxylamine itself. When pure, it may be preserved for a considerable time, but gradually becomes yellow, and acquires a smell something like that of piperidine. It does not appear to have any of the explosive properties which are characteristic of hydroxylamine. It burns with a faintly luminous flame and without deflagration, and is not decomposed by percussion. Hydriodic acid reduces it to ethylamine. Hydrochloric acid at 300° decomposes it with formation of ammonia, and probably of acetaldehyde, but the latter was not actually found among the products of the reaction. The salts with hydrochloric and sulphuric acids are oils, and could not be obtained in the solid form. The acid *oxalate* crystallises from water in small plates melting at 95—97°, and is readily soluble in alcohol.

β-Ethylhydroxylamine reacts with 1 mol. of phenylic isocyanate forming a compound, the formula of which is probably

NHPh·CO·NEt·OH.
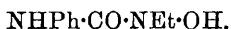
It forms transparent crystals, melts at 98°, decomposes at 145°, and in alcoholic solution gives a dark bluish-violet coloration with ferric chloride. It is not affected by aqueous soda in the cold, but decomposes when heated, symmetrical diphenylcarbamide, aniline, carbonic anhydride, and *β*-ethylhydroxylamine being formed.

β-Methylhydroxylamine is prepared in a manner similar to the ethyl derivative, which it resembles in its general properties. The last portion of the distillate obtained during the preparation is redistilled, and the base then passes over as a colourless liquid, which, when cooled or shaken, solidifies in long, colourless prisms. When rapidly heated in a

wide melting point tube, it melts at 42°, and solidifies again at 20°, but a thermometer immersed in the substance shows a temperature of 36° for the melting point. It deliquesces in the air forming a liquid which rapidly evaporates. Like the ethyl derivative, it has no explosive properties ; it is reduced by hydriodic acid to the corresponding amine, and is decomposed by hydrochloric acid. Of the salts, the hydrochloride and zinc chloride compound have been previously described by Dittrich (*Ber.*, **23**, 599), and by Crismer (Abstr., 1890, 558). The *sulphate* is an oil, the *oxalate* only crystallises with difficulty, and the tartrate could not be obtained in the solid form. The *picrate* forms small, yellow tablets, melts at 128—130°, and dissolves very readily in water and alcohol. The free base combines with 1 mol. of phenylic isocyanate to form a substance of the formula $NHPh \cdot CO \cdot NMe \cdot OH$; this crystallises from hot light petroleum in small tablets melting at 93—94° with decomposition. In its chemical properties it resembles the corresponding derivative of the ethyl compound.

Hydroxylamine reacts with 1 mol. of phenylic isocyanate to form a white powder, which is only slightly soluble in the usual solvents, and melts at 144° with decomposition. This substance has a reducing action, gives a bluish-violet coloration with ferric chloride in alcoholic solution, and is not altered by aqueous soda in the cold ; on boiling, however, diphenylcarbamide, aniline, carbonic anhydride, and hydroxylamine are formed. It is, therefore, most probably *symmetrical phenylhydroxycarbamide*, $NHPh \cdot CO \cdot NH \cdot OH$. It reacts with a second molecule of phenylic isocyanate to form a substance which melts at 178° with decomposition, and gives a cherry-red coloration with ferric chloride ; this substance is probably *diphenylhydroxybiuret*, $NHPh \cdot CO \cdot N(OH) \cdot CO \cdot NHPh$, and the fact that such a compound is formed from hydroxylamine, but not from ethyl- or methyl-hydroxylamine, is an additional proof that the last two contain the alkyl group combined with the nitrogen atom.　　　　　A. H.

Thiocarbamides. By H. SALKOWSKI (*Ber.*, **26**, 2497—2506 ; compare Abstr., 1891, 1474).—On heating methylamine thiocyanate and ethylamine thiocyanate, they are readily converted into the corresponding thiocarbamides, which are extremely soluble ; it is for this reason that their formation was not previously observed. The amount of thiocarbamide formed increases as the temperature rises, and is also dependent on the length of time during which the heating is continued. The quantity of bye-products also increases with the temperature. The thiocarbamide was determined by conversion into sulphide ; the needful precautions, and the separation of silver sulphide from silver thiocyanate, are fully described. The author replies to Mazzara's recent criticisms (Abstr., 1893, i, 411) on his previous paper ; the chief questions at issue are certain discrepancies in the melting points of several compounds. Diethylamine thiocyanate and dimethylamine thiocyanate are converted by heat into the corresponding thiocarbamides ; the reaction appears to be independent of the temperature (130—150°) and of the time ; the diethylamine salt undergoes change less readily than the dimethylamine

derivative, but, in both cases, it is much less complete than with the salts of the primary amines. Dimethylthiocarbamide, $NMe_2 \cdot CS \cdot NH_2$, is deposited from water in prisms ; it melts at 159°, and is not altered on exposure to air. These results are at variance with the observations of Spica and Carrara, who describe this compound as deliquescent, and melting at 81—82°. Diisobutylamine thiocyanate and diisoamylamine thiocyanate cannot be converted into the thiocarbamides by heat, as the reaction proceeds with even greater difficulty than in the case of the diethylamine salt.   J. B. T.

Formaldehyde. By G. PULVERMACHER (*Ber.*, **26**, 2360—2363).— With hydrazine hydrate, formaldehyde yields *formalazine*, $C_2H_4N_2$. This is a very insoluble, amorphous substance, readily hydrolysed by mineral acids to formaldehyde and salts of hydrazine. No pure hydrochloride could be isolated, but a *platinochloride*, $(C_2H_4N_2)_6, H_2PtCl_6$, was prepared. Formalazine is reduced by zinc and acetic acid to ammonia and methylamine ; no symmetrical dimethyhydrazine could be found among the products.   C. F. B.

Separation of Volatile Fatty Acids. By M. WECHSLER (*Monatsh.*, **14**, 462—469).—Two fatty acids, in molecular proportion, were dissolved in water, neutralised to the extent of four-fifths with soda, the remaining acid distilled over with steam, enough sulphuric acid added to the residue to liberate three-fourths of the combined acids, the liberated acids distilled over, and the remaining acid finally liberated with sulphuric acid, and distilled over. The mixtures investigated were formic and acetic, acetic and propionic, acetic and butyric, acetic and isobutyric, propionic and butyric, butyric and isovaleric, butyric and caproic. The first fraction always contained the acid of greater molecular weight ; the last that of less molecular weight ; both in a nearly pure condition, except in the case of the mixture of butyric and isovaleric acids, when no separation was effected by the above method.   C. F. B.

Preparation of Silver Formate. By E. J. MAUMENÉ (*Bull. Soc. Chim.*, [3], **9**, 580—584).—When silver nitrate and sodium formate solutions are mixed in equivalent proportions, the precipitate is a double sodium silver formate, and precipitation is gradual and incomplete. In presence of excess of silver nitrate, the double salt is slowly converted into silver formate, but some decomposition takes place at the same time, silver and silver hydride being formed. The author considers that these phenomena could be predicted from his "general laws."   C. H. B.

Preparation of Methylethylpropionic acid, and Determination of the Solubilities of its Calcium, Barium, and Silver Salts. By V. KULISCH (*Monatsh.*, **14**, 559—571).—This acid is prepared by the interaction of secondary butylic iodide, diethylic malonate, and sodium ethoxide, and subsequent treatment of the resulting secondary diethylic butylmalonate with potash, whereby secondary butylmalonic acid is obtained, crystallising in large plates and melting at 76°. On heating in a reflux apparatus until no more

carbonic anhydride is evolved, it yields the acid, $CHMeEt\cdot CH_2\cdot COOH$, which boils constantly at 196—198°. The *calcium salt*, $(C_6H_{11}O_2)_2Ca + 3H_2O$, crystallises in felted masses of prismatic needles, and has the solubility $s = 12\cdot642 + 0\cdot31185(t-1) - 0\cdot00383(t-1)^2$. The *barium salt*, $(C_6H_{11}O_2)_2Ba + 3\frac{1}{2}H_2O$, crystallises badly. Its solubility is given by the expression $s = 11\cdot711 - 0\cdot33372t + 0\cdot00464t^2$. The *silver salt* is a white, amorphous powder, having the solubility $s = 0\cdot8803 - 0\cdot00287t + 0\cdot000066t^2$. G. T. M.

Oxidation and Constitution of Erucic acid. By M. Fileti and G. Ponzio (*J. pr. Chem.*, [2], **48**, 323—336).—One of the authors has already indicated the results which are obtained by oxidising erucic acid with nitric acid (Abstr., 1893, i, 551). Calcium nonylate crystallises with $1H_2O$, and the magnesium salt with $1\frac{1}{2}H_2O$; the cadmium salt melts at 91—92°, not 96°.

The nitrogenous compound, previously referred to (*loc. cit.*), is *dinitrononane*, $CH_2Me\cdot[CH_2]_6\cdot CH(NO_2)_2$; it is a slightly yellow liquid, which is heavier than water; in the oxidation of erucic acid it is a very minor product, only amounting to some 0·3 per cent. of the erucic acid. The *potassium* derivative, $C_9H_{17}KN_2O_4$, and the *ammonium* derivative are described.

In order to assure themselves that the non-volatile acid which they obtained along with brassylic acid was arachic acid and not behenic acid, the authors prepared the amide, and compared it with arachamide, which they found to melt at 108° (Scheven and Gössman, *Annalen*, **97**, 262, give 98—99°); and with *behenamide*, which melts at 84°; the amide was identical with arachamide. *Brassylamide* melts at 177°.

Thus nonylic and brassylic acids are the chief products of the oxidation of erucic acid by nitric acid, small quantities of dinitrononane and arachic acid being also formed. 1 mol. of erucic acid is thus oxidised to 1 mol. of nonylic and 1 mol. of brassylic acid. This indicates that the double linking in erucic acid occurs between the 13th and 14th carbon atoms from the carboxyl group, giving the formula

$$CH_2Me\cdot[CH_2]_6\cdot CH\dot{:}CH\cdot[CH_2]_{11}\cdot COOH.$$

Some remarks on Baruch's paper (Abstr., 1893, i, 551) are given in conclusion. A. G. B.

Oxybehenic acid. By M. Fileti (*J. pr. Chem.*, [2], **48**, 336—344).—The method of obtaining this acid has already been indicated (Abstr., 1893, i, 551); it appears to be identical with the acid obtained by Holt and Baruch by the action of strong sulphuric acid on behenolic acid (Abstr., 1893, i, 393), this resemblance being maintained in the derivatives as well as in the acids themselves. The ethylic salt melts at 54°. The author gives several possible formulæ for oxybehenic acid, but he cannot regard the problem of its constitution as solved. A. G. B.

Lagic acid. By C. Böttinger (*Ber.*, **26**, 2327—2329; compare Abstr., 1891, 1061).—The author has failed to obtain crystalline lagic

acid ; it may, however. be purified by precipitation with light petr-
oleum from ethereal solution ; galic acid is first thrown down, then
lagic acid, and finally a colourless, crystalline acid (see below).
Lead acetate may be used to approximately separate lagic acid
from galic acid, lead galate being first precipitated. *Lead lagate*,
$(C_4H_3O_3)_2Pb$, forms a pale yellow, voluminous precipitate which
rapidly changes to dense, white crystals on heating. *Aniline lagate*
and *dimethylaniline lagate* are not characteristic. With phenyl-
hydrazine, lagic acid yields a compound which, after treatment with
ether, forms yellow crystals melting at 108° ; it undergoes decom-
position on heating with hydrochloric acid, or acetic acid, phenyl-
hydrazine being eliminated. The *lead salt*, $(C_{10}H_9N_2O_2)_2Pb$, is
yellow. The remaining products of the reaction have not yet been
fully investigated. Lagic acid is completely decomposed by the
action of bromine and water at 100° under pressure, carbonic
anhydride, bromoform, and other bromine derivatives of hydro-
carbons being formed.

The crystalline acid (see above) was only obtained in very small
quantity ; it becomes transparent at 171°, sublimes and melts at 178°,
and at higher temperatures vapour is evolved which induces tears.
It is readily soluble in water, and behaves like lagic acid when treated
successively with copper sulphate, ammonia, and acetic acid. The *lead
salt* is colourless and crystalline. The *silver salt* readily dissolves in
water and ammonia.   J. B. T.

Constitution of Dicyanides of Dimolecular Acids. By L.
BOUVEAULT (*Bull. Soc. Chim.*, [3], **9**, 576—578).—The dicyanides of
dimolecular acids (Abstr., 1893, i, 553) in alkaline solution split up
into hydrocyanic acid and the acid corresponding with the anhydr-
ide from which they were prepared ; phenylhydrazine produces a
similar decomposition, but with formation of a hydiazide. In pre-
sence of concentrated hydrochloric acid, however, the products are a
substituted tartronic acid and the acid corresponding to the an-
hydride. The author considers that these changes can be explained
in a similar way to the bipolymerisation of nitriles. Two molecules
of the acid cyanide $R \cdot CO \cdot CN + R \cdot CO \cdot CN$ yield the dicyanide
$\begin{array}{c} O-CR \cdot CN \\ | \quad | \\ N=C \cdot CO \cdot R \end{array}$, or, in other words, the cyanides of the dimolecular acids
are internal anhydrides of the monoximes of cyanohydroxy-α-dike-
tones $R \cdot CO \cdot C(NOH) \cdot CR(OH)CN$, and it is easy to see that a com-
pound of this type may decompose into an acid of the type $R \cdot COOH$
and a nitrile of a substituted tartronic acid $N:C \cdot CR(OH)CN$, the
latter immediately undergoing saponification.   C. H. B.

Action of Ethylic Bromalkylmalonates on Ethylic Sodio-
malonate. By S. RUHEMANN (*Ber.*, **26**, 2356—2358).—Ethylic
bromomethylmalonate with ethylic sodiomalonate yields, for the most
part, dicarbotetracarboxylic acid, the *phenylhydrazide* of which,
$C_4(CO \cdot N_2H_2Ph)_2$, is a white, crystalline powder decomposing at 255°,
and ethylic methylmalonate is also formed. Ethylic bromethyl-
malonate exhibits an analogous reaction.   C. F. B.

Behaviour of Maleïc acid when heated. By Z. H. SKRAUP *(Monatsh.*, **14**, 501—504).—Experiments are described which show, in contradiction of Tanatar (Abstr., 1893, i, 193). that inactive malic acid is formed along with fumaric acid (and maleïc anhydride) when maleïc acid is heated. Beilstein has adopted Tanatar's erroneous statement in the last edition of his *Handbuch.* C. F. B.

Synthesis of Teraconic acid. By H STOBBE *(Ber.*, **26**, 2312— 2319).—Teraconic acid, $COOH\cdot CH_2\cdot C(COOH):CMe_2$, is prepared by the action of sodium ethoxide (2 mols.) on a mixture of diethylic succinate (1 mol.) and acetone (2 mols.) in absolute ether at low temperatures ; the product is dissolved in ice-cold water, and the sodium salt decomposed by dilute sulphuric acid ; on extraction with ether, a mixture of two acids is obtained, which can be separated by treatment with benzene, in which teraconic acid is insoluble. The teraconic acid was identified by its properties and those of its calcium and barium salts, and also by its conversion into terebic acid. The yield is 55 per cent. of the theoretical. The author considers that the condensation of acetone and diethylic succinate proceeds in a manner similar to that of succinic acid and aldehydes as observed by Fittig and his scholars, and that the formation of teraconic acid is preceded by that of a hypothetical ethylic diaterebate, $COOEt\cdot CH_2\cdot CH(COOEt)\cdot CMe_2\cdot OH$. The second acid, which is readily soluble in benzene, is being further investigated. Ethylic succinosuccinate was the only product which could be obtained by the action of sodium, or of sodium ethoxide, on a mixture of ethylic acetate and ethylic succinate. J. B. T.

Action of Sodium Ethoxide on Ethylic Dibromosuccinate. By G. PUM *(Monatsh.*, **14**, 491—500 ; compare Abstr., 1888, 1058). —The product of the action of sodium ethoxide (2 mols.) on ethylic dibromosuccinate (1 mol.), in absolute alcoholic solution, contains 87 per cent. of ethylic ethoxymaleate, the remainder being ethylic acetylenedicarboxylate. By cautiously hydrolysing the product with alcoholic potash and adding the calculated amount of acetic acid and crystallising, potassium hydrogen acetylenedicarboxylate was first obtained, and then *potassium hydrogen ethoxymaleate*, which crystallises in thin plates. The *acid* itself, $COOH\cdot CH:C(OEt)\cdot COOH$, forms minute, white needles which melt at 144—147°.

When the crude product above mentioned is dissolved in chloroform, it takes up bromine, and the quantity of ethylic dibromomaleate isolated from this was such as to show that it had been formed from the ethoxymaleate as well as from the acetylenedicarboxylate. C. F. B.

Isomerism in the Mucic acid Series. By Z. H. SKRAUP *(Monatsh.*, **14**, 470—490).—Ethylic mucate (which melts at 172°, and not at 158° as the text-books assert, and forms a crystalline compound, $COOEt\cdot[CH\cdot OH]_4\cdot COOEt + CaCl_2$, with calcium chloride), when boiled for one hour with acetic chloride, yields *ethylic α-tetracetylmucate*, melting at 189° ; if heated for four hours at 100°

with acetic chloride in a sealed tube, it yields an isomeric β-compound which melts at 122°, is much more soluble in acetone than the α-isomeride, and is much more readily hydrolysed by alcoholic soda. The latter can be partially converted into the β-variety by heating it with an acetic acid solution of hydrogen chloride. Both substances are optically inactive, and both yield mucic acid, melting at 225° (the text-books give a wrong melting point). when hydrolysed with mineral acids. The same acid is also obtained, but in small amount, when the hydrolysis is effected by means of alkalis, the main product consisting of a syrupy mixture of two *acids* identical in composition with mucic acid, and of which the *calcium salts* are amorphous, and have respectively the composition $C_6H_8O_8Ca + 3H_2O$ and $C_6H_8O_8Ca + 2H_2O$. Alcoholic ammonia attacks both α- and β-tetracetylmucates, the latter the more readily, and among the products mucamide was identified. Benzylamine converts the β-compound into *ethylic tetracetylbenzylmucamate,*

$$COOEt \cdot [CH \cdot OAc]_4 \cdot CO \cdot NH \cdot CH_2Ph,$$
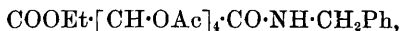
melting at 182—184°, and an oil, the latter in larger amount; the α-compound yields a similar oil, but no crystalline compound.

Benzoic chloride, under the same circumstances as acetic chloride, does not form two isomeric derivatives of ethylic mucate; *ethylic di-* and *tetra-benzoylmucate,* melting respectively at 174° and 124°, are obtained.

Mucic acid itself, when heated with acetic anhydride and a few drops of concentrated sulphuric acid, yields one *tetracetylmucic acid* only; this melts at 242—243°, and crystallises with 2 mols. either of water or alcohol. *Monacetylmucic acid* was found in the mother liquors from the preparation of ethylic α- and β-tetracetylmucates; it melts at 198°, and crystallises with $1H_2O$ in white prisms.

<div align="right">C. F. B.</div>

The Thiophen Group. By J. MARCUSSON (*Ber.*, **26**, 2457—2465).—The author has been unable to obtain thiophen derivatives having a halogen or nitro-group in the ortho-position to a CO group.

Phenyl thienyl ketone is most easily obtained by exposing a mixture of thiophen, aluminium chloride, and excess of benzoic chloride to direct sunlight. It boils at 300°, and solidifies in needles.

Dibromothienyl phenyl ketone, $C_4SHBr_2 \cdot COPh$ [= 2 : 3 : 5], is obtained by allowing the ketone to remain for some time in contact with excess of bromine. It crystallises in beautiful white needles, and melts at 80°. The *oxime* forms slender needles, melts at 176°, and is soluble in sodium hydroxide. The oxime is not altered by boiling with concentrated sodium hydroxide, but when warmed with acetic anhydride, it yields an *acetyl compound,* which crystallises in slender needles, and melts at 109°.

Dibromothienyl phenyl ketone is scarcely acted on when allowed to remain with excess of bromine for eight days at the ordinary temperature; when heated at 100°, it yields tetrabromothiophen. When mixed with cold fuming nitric acid, it yields metanitrobenzoic and benzoic acids.

Benzoylethylthiophen, when suspended in bromine water and

treated with bromine at 0°, is completely converted into tetrabromothiophen. A *monobromo-compound*, $C_4SHEtBr \cdot COPh$ [= 2 : 3 : 5], is obtained by shaking benzoylethylthiophen with bromine water and subjecting the product to steam distillation. It is a yellow oil which is converted into tetrabromothiophen by the further action of bromine.

Nitrobenzoylethylthiophen, $COPh \cdot C_4SHEt \cdot NO_2$, is obtained by gradually adding fuming nitric acid to the ketone and cooling with water. It crystallises in pale yellow needles, melts at 117°, and gives a beautiful violet coloration with sodium hydroxide in alcoholic solution. The nitro-group is not eliminated by boiling with hydroxylamine and alcoholic potash.

Dibromothiophencarboxylic acid, when heated with excess of bromine in a sealed tube at 100°, is converted into tetrabromothiophen. E. C. R.

Action of Sodium on Orthodibromobenzene. By W. HOSAEUS

(*Monatsh.*, **14**, 323—332).—Goldschmiedt has shown that by the action of sodium on metadibromobenzene and paradibromobenzene, substances of the formula $C_{78}H_{52}Br_2$ are formed (*Monatsh.*, 1886, 541). When orthodibromobenzene, dissolved in ether, is boiled with metallic sodium for about 200 hours, a substance of the same formula is obtained, to which the author gives the name of *orthotridecaphenylene dibromide*. It is a yellow, amorphous powder, which softens at about 245°, and melts at 280—290°. Like the isomeric substances obtained by Goldschmiedt, it is insoluble in alcohol, and readily soluble in benzene, chloroform, and carbon bisulphide, but differs from them in being soluble in ether. It was found impossible to obtain any further condensation, either by the action of sodium or heated magnesium on the compound. The molecular weights of all three substances were determined by the boiling-point method, benzene being used as the solvent. In each case the molecular weight was found to correspond with the formula $C_{78}H_{52}Br_2$. Schiff's method for the preparation of orthodibromobenzene (Abstr., 1891, 44) was employed, but orthodibromaniline sulphate, instead of the free base, was diazotised in alcoholic solution by means of ethylic nitrite. In this way, a yield of 50 per cent. of the theoretical was obtained. A. H.

Parachlorobromocymene and its Oxidation Products. By

G. PLANCHER (*Gazzetta*, **23**, ii, 68—75).—On heating parabromothymol with phosphorus pentachloride at 160—200°, neutralising, with sodium carbonate, and distilling the product in a current of steam, parachlorobromocymene passes over, whilst *tribromothymyl phosphate*, $(C_{10}H_{12}Br)_3PO_4$, remains; the latter can be purified by crystallisation from a mixture of alcohol and ether, and forms opaque, acicular crystals, melting at 94—95°.

Parachlorobromocymene is also obtained by brominating, in presence of iodine, the chlorocymene prepared from thymol; it is a colourless, almost odourless, highly refractive liquid, which boils at 259—261°

under a pressure of 750·86 mm. On oxidation with dilute nitric acid, it yields *chlorobromoterephthalic acid*,

$$C_6H_2BrCl(COOH)_2 \text{ [Br : Cl : (COOH)}_2 = 1 : 4 : 2 : 5],$$
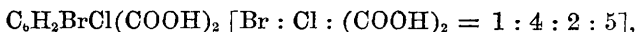
which is purified by crystallisation from acetic acid; it forms long, lustrous needles, begins to sublime at 240°, and melts at 308—310° (corr.), with slight decomposition. It is soluble in alcohol and acetic acid, but only sparingly in boiling water and benzene; the *diethylic* salt melts at 115—116·5°. The products of oxidation also contain *chlorobromoparatoluic acid*, $C_6H_2MeBrCl·COOH$ [Br : Cl : Me : COOH = 1 : 4 : 2 : 5], and a *chlorobromocumic acid* (?), which are best separated by distillation in a current of steam; the latter acid forms small prisms melting at 124—128°, but was not obtained in sufficient quantity for complete examination. The former acid separates from acetic acid in small, silky crystals melting at 185—187°; it is soluble in alcohol or acetic acid, but only sparingly so in benzene, petroleum, or water.   W. J. P.

Elimination of Halogens from Substituted Phenols. By F. W. Schlieper (*Ber.*, **26**, 2465—2471; compare Abstr., 1892, 704).—*Chlorometanitrophenol* is prepared by passing dry chlorine over finely-divided metanitrophenol; it does not crystallise from the usual solvents, and, after washing with water and drying, melts at 120°. When warmed with stannous chloride (6 mols.) and concentrated hydrochloric acid, it yields *chlorometamidophenol*, which melts at 85—87°.

Chloronitroanisoil is prepared by the interaction of chloronitrophenol, sodium methoxide, and methylic iodide. It crystallises in bright yellow needles, melts at 90°, and, on reduction, yields chloranisidine.

Iodometanitrophenol is obtained by adding powdered iodine and mercurous oxide to an acetic acid solution of metanitrophenol. It is a bright yellow powder, melts at 134°, and, on reduction, yields met-amidophenol.

Iodonitroanisoïl, prepared in a similar way to the chlorine compound, crystallises in bright yellow needles, melts at 121—122°, and, on reduction, yields metanisidine, which is an oil, and boils at 250—260° (uncorr.).

Bromorthonitrophenol and bromoparanitrophenol, as stated by Brunek and Körner, on reduction, yield bromorthamido- and bromoparamido-phenol respectively.

When the above chloranisidine is diazotised and the diazo-groups are displaced by hydrogen by Friedländer's method, it yields ortho-chloranisoïl, which boils at 198°; from this the author concludes that the above compounds have the constitution OH : halogen : NO$_2$ = 1 : 2 : 3.   E. C. R.

Metanitroorthocresol. By O. Michel and E. Grandmougin (*Ber.*, **26**, 2349—2354).—The mixture of nitroindazole and nitrocresol (containing respectively 30 and 70 per cent. of these substances) obtained by diazotising nitrotoluidine and heating the product (Abstr., 1891, 312) is dissolved in very dilute aqueous soda, and the

solution is saturated with carbonic anhydride, which precipitates the nitroindazole. The nitrocresol remains in solution, and can be precipitated by the addition of mineral acids. It was thus obtained pure, and various derivatives of it were prepared: their melting points differ considerably from those of the same substances, as previously prepared from impure materials (Abstr., 1884, 1006).

Metanitroorthocresol [Me : OH : NO$_2$ = 1 : 2 : 4] crystallises in pale yellow needles melting at 118°; its *acetyl* and *benzoyl* derivatives in lustrous, white needles melting respectively at 74° and 126°. With bromine in acetic acid solution, it yields *dibromonitrocresol*, which crystallises in yellowish needles melting at 115°, and yields an *acetyl derivative* in short, white prisms melting at 127°. By allowing nitrocresol to remain with diazotised nitrotoluidine in cold alkaline solution, *ortho-* and *para-azonitrotoluenenitrocresol*

$$NO_2 \cdot C_6H_3Me \cdot N:N \cdot C_6H_2Me(OH) \cdot NO_2 \quad [Me : N \text{ \&c.} : NO_2 = 1' : 2' : 4']$$

are obtained, and may be separated by crystallisation from aniline and alcohol, in which the para-compound is more soluble. The ortho-compound [Me : OH : NO$_2$: N &c. = 1 : 2 : 4 : 3] crystallises in matted, brown needles, melts with decomposition at 250—260°, and yields an *acetyl derivative* forming brown needles melting at 205°. The para-compound [1 : 2 : 4 : 5] crystallises in lustrous, red needles melting at 260—270°, and its *acetyl derivative*, in orange-yellow needles melting at 211°. C. F. B.

Preparation of Parabromothymol. By G. PLANCHER (*Gazzetta*, **23**, ii, 76—79).—Parabromothymol is conveniently prepared by the direct bromination of thymol in acetic acid solution; the product solidifies when poured into water, and is then purified by precipitating its solution in soda by sulphuric acid. No other compound could be isolated from the product of bromination. W. J. P.

Metadiiodoquinone. By F. KEHRMANN and J. MESSINGER (*Ber.*, **26**, 2377).—Metadiiodoquinone may be obtained by the oxidation of symmetrical triiodophenol by means of chromic acid. The yield is, however, not so good as that given by Siefert's original method of preparation (*J. pr. Chem.*, [2], **28**, 437). A. H.

Phenylallylcarbinol. By H. FOURNIER (*Bull. Soc. Chim.*, [3], **9**, 600—601).—*Phenylallylcarbinol*, $C_3H_5 \cdot CHPh \cdot OH$, is obtained by the action of allylic iodide on benzaldehyde in presence of zinc turnings and dry ether. It is a colourless, somewhat viscous, and highly-refractive liquid, with a feeble, aromatic odour. It boils at 228—229°; sp. gr. at 18° = 1·004; refractive index for D at 17° = 1·534; molecular weight as determined by Raoult's cryometric method, 152 (calc. 148). When heated with acetic anhydride at 180° for three hours, it yields an *acetate*, $C_3H_5 \cdot CHPh \cdot OAc$, which is a colourless liquid boiling at 239—240; sp. gr. at 18° = 1·015. C. H. B.

Action of Nascent Bromine on some Benzene Derivatives. By W. VAUBEL (*J. pr. Chem.*, [2], **48**, 315—322).—This is a con-

tinuation of the author's work on the subject (compare Abstr., 1893, i, 560). The reactions which have been studied are those between nascent bromine and methylaniline, ethylaniline, acetanilide, acet-orthotoluidide, and acetoparatoluidide. respectively. The influence which the various groups concerned in these compounds exert on the entry of the bromine is considered, and illustrated by drawings which represent the author's conception of the benzene nucleus (Abstr., 1891, 1343).   A. G. B.

Reduction of Dinitro-compounds in Alkaline Solution. By E. LELLMANN and J. HAAS (*Ber.*, **26**, 2583—2589).—The behaviour of orthodinitrodibenzylamine and of its phenyl derivative on reduction in alkaline solution has been described (Abstr., 1892, 316, 890; 1893, i, 201). The present experiments deal with the reduction of aliphatic alkyl derivatives of the above-named base.

Orthodinitrodibenzylethylamine, $NEt(CH_2 \cdot C_6H_4 \cdot NO_2)_2$, is obtained by heating on the water bath an alcoholic solution of orthonitro-benzylic chloride with mixed aqueous solutions of ethylamine and soda; the separation of the secondary products and the isolation of the new base is described. It separates from alcohol in large, trans-parent yellow crystals, melts at 56°, and forms sparingly soluble platino- and auro-chlorides. When reduced with zinc dust and alco-holic soda, *orthodiamidodibenzylethylamine* is obtained; this crystallises in white needles, and melts at 94°. *Orthodiamidodibenzylmethylamine*, prepared by reducing the dinitro-base (Gabriel and Jansen, Abstr., 1892, 218), melts at 96°. *Orthodinitrodibenzylpropylamine* melts at 31°, and the *diamido*-base at 112°. *Orthodinitrodibenzylisobutylamine* melts at 62°, and the *diamido*-base melts at 132°. *Orthodinitrodibenzyl-allylamine* melts at 55°, and the *diamido*-base at 104°. *Orthodinitrotri-benzylamine* melts at 82°, the *diamido*-base at 143°. A small amount of *orthodinitrodibenzylorthotoluidine* is obtained by heating together alcoholic solutions of orthotoluidine and orthonitrobenzylic chloride; it melts at 205°.   A. R. L.

Oxidation of Pentamidobenzene. By A. W. PALMER and H. S. GRINDLEY (*Ber.*, **26**, 2304—2307).—Pentamidobenzene hydro-chloride is treated with sodium acetate, and the aqueous solution oxidised for 48 hours by means of a stream of air at the ordinary temperature. The product, which is dark brown and insoluble in the ordinary media, appears to be triamidoquinone or amidodiimido-quinol, $C_6H_7N_3O_2$; it does not melt, but on heating decomposes with evolution of ammonia, is readily soluble in nitric acid, more sparingly in glacial acetic acid and hydrochloric acid with an amber colour; sulphuric acid produces a mahogany colour; with dilute potash or soda, a blue coloration is obtained, which changes after some time. On heating with hydrochloric acid at 130—160° under pressure, although the compound appears to be unaltered, yet one-third of the nitrogen is eliminated as ammonia.

By the action of air on pentamidobenzene hydrochloride in aqueous solution, a compound is formed which contains chlorine, dissolves in

water with a reddish-brown colour, and is precipitated by hydrochloric acid.

Pentamidotoluene hydrochloride, on oxidation in presence of sodium acetate, yields a compound $C_6H_6MeN_3O_2$, which closely resembles the benzene derivative, but is somewhat more soluble. J. B. T.

Organic Salts of Diamidophenol and Triamidophenol. By A. LUMIÈRE and A. SFYEWETZ (*Bull. Soc. Chim.*, [3], **9**, 595—599).— The oxalate and picrate are the only salts of diamidophenol and organic acids that have any special interest. All the others are very unstable, rapidly turn brown, even when their solutions are concentrated in a vacuum, and cannot be isolated in a crystalline form.

Diamidophenol oxalate, $OH \cdot C_6H_3(NH_2)_2, H_2C_2O_4$, forms small, white crystals, almost insoluble in cold, but somewhat soluble in hot, water, very slightly soluble in cold alcohol or ether. It dissolves easily in cold solutions of alkalis or inorganic acids and in hot solutions of organic acids. In presence of sodium or potassium hydroxide, the solution rapidly absorbs oxygen from the air, and becomes red; in presence of ammonia, it becomes dark blue, this reaction being very sensitive. The salt dissolves in aqueous solutions of certain salts that have a feeble alkaline reaction, such as sodium sulphite or acetate, and the solutions with sulphite are energetic developers of photographic plates. A 2 per cent. solution of sodium sulphite dissolves 1·5 per cent. of the oxalate, a 10 per cent. solution dissolves 5·5 per cent., and a saturated (17 per cent.) solution dissolves 7 per cent.

Diamidophenol picrate, $OH \cdot C_6H_3(NH_2)_2, 2C_6H_3N_3O_7$, forms confused, silky, lemon-yellow needles, which alter rapidly in presence of air when moist, but are stable when dry. It melts with decomposition at 120°, is only slightly soluble in cold water, somewhat soluble in alcohol, readily in ether or acetone, but insoluble in benzene. The salt is decomposed by acids, and dissolves in alkalis, the latter solutions absorbing oxygen from the air, and becoming deep red-brown in presence of potash or soda, and deep green in presence of ammonia. At about 120°, it decomposes suddenly with incandescence. Diamidophenol picrate reduces soluble silver salts, but has no special value in photography.

Triamidophenol picrate, $C_6H_2(NH_2)_2, OH \cdot 3C_6H_3N_3O_7$, forms yellow, silky, confused, acicular crystals, only slightly soluble in cold water, but more so in hot, very soluble in alcohol, and also in ether and acetone, forming green solutions in all cases. It is insoluble in benzene, is decomposed by acids, and is only slightly soluble in alkalis. The salt alters very rapidly if exposed to air whilst moist, and becomes deep olive-green, but is stable when dry. It melts with decomposition at about 96—97°, and at about 140—150° decomposes with incandescence. This salt only very slowly reduces soluble silver salts.

Other salts of triamidophenol are obtained by the action of acids on solutions of the sulphite (*loc. cit.*), but the formate, acetate, oxalate, tartrate, and citrate do not crystallise well, and their solutions alter even when concentrated in a vacuum. C. H. B.

Amido-derivatives of Phloroglucinol. By J. POLLAK (*Monatsh.*, **14**, 401—427).—When phloroglucinol is heated with aqueous ethylamine at 110—120° in a sealed tube, *diethylamidohydroxybenzene*, $OH \cdot C_6H_3(NHEt)_2$ [$= 1 : 3 : 5$], is formed; if it is desired to obtain the free base, it is best to allow phloroglucinol to remain for some time in contact with ethylamine at the ordinary temperature and in the absence of air. The base is a crystalline substance melting at 106—108°, and is converted by prolonged boiling with water into phloroglucinol. The *hydrochloride*, $C_{10}H_{16}N_2O,2HCl$, crystallises in colourless, transparent, triclinic tables ($a : b : c = 1·03734 : 1 : 0·6749$; $\alpha = 92° 31\frac{1}{2}'$, $\beta = 96° 41'$, $\gamma = 93° 34'$) melting with decomposition at 199—201°; the *platinochloride*, $C_{10}H_{16}N_2O,H_2PtCl_6 + H_2O$, crystallises in yellow, lustrous needles, decomposing above 130°. A *triacetyl derivative*, $OAc \cdot C_6H_3(NEtAc)_2$, was obtained in white, triclinic plates $a : b : c = 1 : 1·0459 : 1·6598$; $\alpha = 79° 53'$, $\beta = 65° 54'$, $\gamma = 112° 7'$; it distils unchanged, and melts at 92—95° when crystallised from benzene, at 80—85° when crystallised from ether; boiling with water converts it into the *diacetyl derivative*, $OH \cdot C_6H_3(NEtAc)_2$, which forms lustrous, monoclinic prisms $a : b : c = 0·7764 : 1 : 0·3960$; it yields an *ethoxy-derivative*, $OEt \cdot C_6H_3(NEtAc)_2$, melting at 65—67°, and a *dinitroso-derivative*, $OH \cdot C_6H_3(NEt \cdot NO)_2$, crystallising in yellowish-white needles, and melting at 136—138°.

When concentrated ammonia is allowed to remain for 1 to 3 days in contact with phloroglucinol in a sealed tube at the ordinary temperature, *phloramine*, $NH_2 \cdot C_6H_3(OH)_2$, is obtained; it crystallises in white needles, and melts at 146—152°. The *hydrochloride* with H_2O, does not melt below 260°, and yields phloroglucinol on prolonged boiling with water; the *triacetyl derivative* is a white, crystalline powder melting at 119—121°. If phloroglucinol is allowed to remain in contact with concentrated ammonia for 14 days, it is partially converted into 1 : 3 : 5-*diamidohydroxybenzene*,

$$OH \cdot C_6H_3(NH_2)_2 ;$$
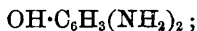
this crystallises in nearly colourless, lustrous prisms, melts at 168—170°, and yields an *acetyl derivative* melting at 201—204°.

As most of the compounds described decompose in air, especially when still impure, many of the operations were performed in an atmosphere of hydrogen.   C. F. B.

Action of Nitrous acid on Amidoparadichlorobenzene. By T. ZETTEL (*Ber.*, **26**, 2471—2473).—A compound which the author believes to be *tetrachlorodiazoamidobenzene* is obtained by adding amylic nitrite to an alcoholic solution of paradichloraniline. It crystallises from light petroleum in beautiful, lustrous prisms, from benzene in slender needles, melts at 170° with decomposition, and is unaltered by boiling with fuming hydrochloric acid, water, or sulphuric acid. When heated with fuming hydrochloric acid in a sealed tube at 130°, it is converted into dichloraniline and tetrachloroquinol. When reduced with stannous chloride and hydrochloric acid, it yields paradichloraniline and a compound which the author believes to be *paradichlorophenylhydrazine*; this crystallises from hot water in

slender, white needles, melts at 105°, and quickly reduces Fehling's solution. The *hydrochloride* crystallises in slender needles.

<div align="right">E. C. R.</div>

Constitution of the Cyanophenylhydrazines and the Triazole Compounds derived from them. By E. BAMBERGER and P. DE GRUYTER (*Ber.*, 26, 2385—2397).—Formazyl methyl ketone,

$$\text{NHPh·N:C(N}_2\text{Ph)·COMe,}$$
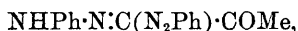
is converted by the action of ammonium sulphide into a base melting at 183°, which has been described by Bamberger and Lorenzen (Abstr., 1893, i, 157). A further study of this substance (details of which will shortly be published) has shown that it has the formula NHPh·N:C(NH$_2$)·COMe. Substances containing the group

$$\text{(NHPh·N:C·NH}_2\text{),}$$
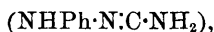
which is analogous to that present in the amidoximes (OH·N:C·NH$_2$), are termed by the authors *amidrazones*, and the base in question therefore receives the name of *acetylamidrazone*. When treated with acetic anhydride, it is converted into phenylacetylmethyl-triazole, $\text{NPh} \diagdown \begin{smallmatrix} \text{N} = \text{C·COMe} \\ \text{CMe:N} \end{smallmatrix}$, which, on oxidation by potassium permanganate in the presence of sodium carbonate, yields phenyl-methyltriazolecarboxylic acid, $\text{NPh} \diagdown \begin{smallmatrix} \text{N} = \text{C·COOH} \\ \text{CMe:N} \end{smallmatrix}$. This acid is identical in every respect with the acid obtained by Bladin (Abstr., 1887, 138) from cyanophenylhydrazine by the action of acetic acid and hydrolysis of the product. Starting from the formula proposed by Bladin for cyanophenylhydrazine, his method of formation leads to a formula for the acid which is different from that which would be assigned to it considering the way in which it is obtained from formazyl methyl ketone, as is shown by a comparison of his formula for methyltriazolecarboxylic

acid, $\text{PhN} \overset{2}{\underset{5}{\diagdown}} \begin{smallmatrix} \text{N} = = = \overset{3}{\text{CMe}} \\ \text{C(COOH):N} \\ \quad 4 \end{smallmatrix}$, with those given above. According to

Bladin, the compound is a 1-phenyl-3-methyl-5-carboxylic acid, whilst, according to the method adopted by the authors, it is a 1-phenyl-5-methyl-3-carboxylic acid.

Similar relations hold with regard to phenyltriazolecarboxylic acid, which has also been prepared by the authors, and found to be identical with that previously obtained by Bladin.

Phenylmethyltriazolecarboxylic acid, when heated at the temperature of its melting point, loses carbonic anhydride, and forms phenyl-methyltriazole; the latter was obtained by Bladin as an oil, but the authors have succeeded in preparing it in the form of crystals melting at 191°. An isomeric substance which melts at 86—87°, and is undoubtedly different from the compound obtained by Bladin and the authors, has been prepared by Andreocci (Abstr., 1892, 636) by the action of phenylhydrazine on acetylurethane, a mode of formation which leads to a formula identical with that ascribed by Bladin to the

substance obtained by him. These inconsistencies are removed if the formation of dicyanophenylhydrazine is regarded as analogous to the production of the amidoximes by the action of hydroxylamine on cyanides: $N:C \cdot CN + NH_2 \cdot NHPh = NHPh \cdot N:C(CN) \cdot NH_2$. Dicyanophenylhydrazine thus becomes *cyanamidrazone*, and the formation of 1-phenyl-5-methyltriazole-3-carboxylic acid is accounted for without difficulty.

The formula proposed for " dicyanophenylhydrazine " is confirmed by the fact that this substance is formed when " flaveanwasserstoff " is treated with phenylhydrazine in alcoholic solution, hydrogen sulphide being evolved. A portion of the "flaveanwasserstoff" is converted by the sulphuretted hydrogen into "rubeanwasserstoff."

A second compound, formed by the combination of phenylhydrazine with cyanogen, is known, to which Senf (*J. pr. Chem.*, **35**, 535) has given the name cyanophenylhydrazine, and the formula $NH_2 \cdot NPh \cdot C(NH) \cdot C(NH) \cdot NPh \cdot NH_2$. This compound has been synthesised by the authors in two different ways, both of which lead to the formula $N_2HPh \cdot C(NH_2) \cdot C(NH_2) \cdot N_2HPh$, according to which it is *diamidrazone*.

1. It is formed when " rubeanwasserstoff " is treated in alcoholic solution with phenylhydrazine, hydrogen sulphide being evolved.

2. The same substance is produced by the action of phenylhydrazine on a solution of cyanamidoxime, $NOH:C(NH_2) \cdot C(NH_2):NOH$, in acetic acid. This reaction is quite analogous to that in which the isonitroso-group of the oximes is replaced by the hydrazone group by the action of phenylhydrazine.

This view of the constitution of the triazole derivatives will of course necessitate a change in the nomenclature of the compounds prepared by Bladin, the nature of which is apparent from a consideration of the formulæ given above (compare this vol., i, 58).

A. H.

Acidyl Derivatives of β-Benzylhydroxylamine. By E. BECK-MANN (*Ber.*, **26**, 2631—2634).—*Dibenzoyl-β-benzylhydroxylamine*, $CH_2Ph \cdot NBz \cdot OBz$ (this vol., i, 27), is prepared by treating β-benzylhydroxylamine with benzoic chloride in presence of aqueous alkali; it crystallises in leaflets, melts at 96—97°, and gives no coloration with ferric chloride. *ββ-Benzoylbenzylhydroxylamine*, $CH_2Ph \cdot NBz \cdot OH$, is obtained when β-benzylhydroxylamine hydrochloride is treated in ethereal solution with sodium carbonate, the solution dried, and benzoic chloride added; it melts at 106°, and its alcoholic solution gives a red coloration with ferric chloride. *α-Benzoyl-β-benzylhydroxylamine*, $CH_2Ph \cdot NH \cdot OBz$, is formed as already stated (Abstr., 1893, i, 706), by the action of benzoic chloride on *n*-benzylaldoxime; the hydrochloride melts at 147°.

Diacetyl-β-benzylhydroxylamine, $CH_2Ph \cdot NAc \cdot OAc$, obtained by boiling β-benzylhydroxylamine hydrochloride with acetic chloride, is an oil; when treated with sodium ethoxide, it yields *ββ-acetylbenzylhydroxylamine*, $CH_2Ph \cdot NAc \cdot OH$, which melts at 124°. *α-Acetyl-β-benzylhydroxylamine*, $CH_2Ph \cdot NH \cdot OAc$, is obtained in an analogous manner to the corresponding benzoyl compound; the *hydrochloride* melts at 102—103°.

When benzoic chloride is added to an ethereal solution of α-benzyl-hydroxylamine, a compound, probably *α-benzyl-β-benzoylhydroxyl-amine*, $CH_2Ph \cdot O \cdot NHBz$, is formed; it melts at 102—103°, and its ethereal solution gives no coloration with ferric chloride. When the last-mentioned compound is boiled with benzoic chloride, a substance melting at 60—65° is obtained; it is probably the *dibenzoyl* derivative, $CH_2Ph \cdot O \cdot NBz_2$.   A. R. L.

Ethers of Quinoneoxime (Paranitrosophenol). By J. L. BRIDGE (*Annalen*, **277**, 79—104).—The author's experiments, a portion of which have already been described (Abstr., 1892, 1456), show that paranitrosophenol is identical with quinoneoxime; the compound is not tautomeric, and the quinoneoxime formula completely explains its reactions.

The *dibromide* of quinonemethoxime (*loc. cit.*),

$$CO \diagdown \substack{CH = CH \\ CHBr \cdot CHBr} \diagup C:NOMe,$$

is colourless, and melts at 123°; the *dichloride* resembles it, melts at 93°, and, when boiled with dilute alcohol, decomposes into two isomeric chloroquinonemethoximes melting at 123° and 97°. These compounds are also formed by treating chloroquinone with α-methylhydroxyl-amine hydrochloride; it has yet to be decided which of the two theoretically possible formulæ is to be assigned to each of them. Proof that paranitrosophenol is identical with quinoneoxime is furnished by the fact that the nitroso-compound when heated with acetic anhydride yields quinoneacetoxime (m. p. 107°).

Quinonebenzyloxime, $O:C_6H_4:NO \cdot CH_2Ph$, is obtained as already described (*loc. cit.*), or by treating quinone in aqueous solution with α-benzylhydroxylamine; it crystallises from light petroleum in yellow tables, and melts at 63·5°. The *dichloride*,

$$CO \diagdown \substack{CH = CH \\ CHCl \cdot CHCl} \diagup C:NO \cdot CH_2Ph,$$

forms colourless, rhombic tables, melts at 64°, and exhibits great stability towards boiling dilute alcohol; the *dibromide* resembles it. and melts at 68°.

Quinonebenzoyloxime (m. p. 172—174°; *loc. cit.*) forms a *dichloride*, $CO \diagdown \substack{CH = CH \\ CHCl \cdot CHCl} \diagup C:NOBz$, which crystallises in colourless prisms, melts at 165°, and, when boiled with 50 per cent. alcohol, yields a mixture of two isomeric chloroquinonebenzoyloximes; these melt at 197° and 162° respectively. In order to determine the constitution of these compounds, Kehrmann's metachloroquinoneoxime (m. p. 140°: *Ber.*, **21**, 3315) was treated with benzoic chloride; the product was a mixture of the two last-mentioned benzoyl derivatives, thus (according to the author) proving Kehrmann's compound to be itself a mixture, and destroying the value of his conclusions (*loc. cit.*).

Quinonebenzoyloxime dibromide forms colourless prisms, and melts at 145—146° with decomposition; when boiled with dilute alcohol, it yields two *bromoquinonebenzoyloximes* melting at 158° and 171° respectively.

When quinoneoxime in alcoholic solution is treated with bromine, two, or perhaps three, products are formed. One of them, a *dibromo-quinoneoxime*, melts at 170° with decomposition, and the corresponding *benzoyloxime* melts at 191°.

When sodium paranitrosodiphenylamine is treated with benzoic chloride, it yields a benzoyl derivative melting at 156°, and when it is treated with ethylic chlorocarbonate, it yields a carbethoxy-derivative melting at 89°. The constitutions of both these compounds have yet to be determined.   A. R. L.

Compounds containing the Group $C_2N_2O_2$. By A. ANGELI *(Gazzetta,* **23**, ii, 21—37; compare Abstr., 1893, i, 355).—Dibenzoyl-azoxazole forms small, yellow, orthorhombic crystals, $a : b : c = 0.8218 : 1 : 1.3104$.

On oxidising the dinitroso-derivatives of peroxide of isosafrole or isoapiole, or of their bromo- or nitro-derivatives, with alkaline permanganate, acidifying the solution with sulphuric acid, and repeatedly extracting with ether, an *acid,* having the constitution $\begin{matrix} CMe\!-\!\underset{|}{C}\!\cdot\!COOH \\ N\!\cdot\!O\!\cdot\!O\!\cdot\!N \end{matrix}$,

is ultimately obtained. It separates from benzene in large, colourless, flat, monosymmetric needles which contain solvent of crystallisation, and melt at 47°; $a : b : c = 1.7392 : 1 : 0.6207$; $\beta = 87°\ 1'$. When crystallised from water, it melts at 62°, and when obtained free from the solvent, it melts at 92°. It is very soluble in water, alcohol, ether, or ethylic acetate, but less so in benzene, chloroform, or light petroleum. The same acid is obtained by oxidising methylsyngly-oximecarboxylic acid (Abstr., 1884, 1120; 1892, 1175) with nitric acid (sp. gr. 1.45). The *silver* salt is a white powder which blackens in the air, explodes on percussion, and deflagrates on heating.

                                                           W. J. P.

Diisonitrosobromisosafrole. By E. LEVI *(Gazzetta,* **23**, ii, 37—42; compare Abstr., 1893, i, 196, 261).—*α-Diisonitrosobromisosafrole,* $CH_2:O_2:C_6H_2Br\cdot C(NOH)\cdot CMe:NOH$, is formed on reducing its peroxide with zinc-dust and acetic acid in alcoholic solution; it is eventually obtained in beautiful, colourless, lustrous crystals melting at 186°. When heated above its melting point, it decomposes, so that it could not be converted into the β-isomeride by this means. It is very soluble in alcohol or ethylic acetate, but only sparingly so in benzene or light petroleum. The *diacetyl* derivative forms large, white scales melting at 147°; it dissolves in the ordinary solvents, and is partially hydrolysed by potash in the cold.

Diisonitrosobromisosafrole anhydride, $O{<}\begin{matrix} N:C\cdot C_6H_2Br:O_2:CH_2 \\ \underset{|}{N:CMe} \end{matrix}$, is obtained by brominating diisonitrososafrole anhydride in acetic acid solution; it melts at 120—121°, and is insoluble in potash.

Diisonitrosonitroisosafrole anhydride, $O{<}\begin{matrix} N:C\cdot C_6H_2(NO_2):O_2:CH_2 \\ \underset{|}{N:CMe} \end{matrix}$, is prepared by direct nitration; it crystallises in beautiful, lustrous prisms melting at 101—102°, and is a very stable substance.   W. J. P.

Salicylaldoxime. By E. BECKMANN (*Ber.*, **26**, 2621—2631).—Hantzsch has shown that the ortho-substituted aldoximes, which appear to be incapable of intramolecular change into stereoisomerides, have the β- (anti-) configuration.

Action of acetic anhydride, and of acetic chloride, on salicylaldoxime (see Lach, Abstr., 1884, 1154; Claisen and Stock, Abstr., 1891, 451). *Benzoylsalicylonitrile*, CN·C₆H₄·OBz, is obtained by heating salicylaldoxime with benzoic chloride over a free flame; it crystallises in long needles, melts at 105°, and yields salicylonitrile on hydrolysis with alcoholic soda.

Salicylobenzoyloxime, OH·C₆H₄·CH:NOBz, is prepared by gently warming, at about 60°, salicylaldoxime with benzoic chloride; it crystallises in needles, and melts at 117°. On treatment with alcoholic soda, salicylaldoxime is regenerated, but when the compound is heated alone, salicylonitrile is formed.

Benzoylsalicylaldoxime, OBz·C₆H₄·CH:NOH, is formed by heating benzoylsalicylaldehyde with hydroxylamine; it forms white needles, melts at 130°, and, when heated with benzoic chloride, yields benzoylsalicylonitrile.

Dibenzoylsalicylaldoxime, OBz·C₆H₄·CH:NOBz, is obtained by benzoylating salicalylaldoxime by the Schotten-Baumann method; it melts at 126°.

When salicylaldoxime is benzylated with sodium ethoxide and benzylic chloride, besides the monobenzyloxime (m. p. 62—63°), the *dibenzyl derivative*, CH₂Ph·O·C₆H₄·CH:N·O·CH₂Ph is also formed; it melts at 34°. When the monobenzyl derivative is benzoylated, the *compound* OBz·C₆H₄·CH:NO·CH₂Ph is formed; it melts at 47°.

n-Benzylsalicylaldoxime, $OH \cdot C_6H_4 \cdot CH < \begin{smallmatrix} N \cdot C_7H_7 \\ | \\ O \end{smallmatrix}$, prepared by the condensation of salicylaldehyde and β-benzylhydroxylamine, crystallises in pale yellow needles, and melts at 101—102°. When treated in alcoholic solution with benzoic chloride and sodium carbonate, it yields the *benzoyl* derivative, melting at 150°; when the latter or the *n*-benzylsalicylaldoxime is heated with benzoic chloride, *benzylbenzoylsalicylamide*, OBz·C₆H₄·CO·NH·CH₂Ph is obtained; it crystallises in white needles, melts at 114°, and when treated with sodium ethoxide, yields *benzylsalicylamide*, OH·C₆H₄·CO·NH·CH₂Ph, melting at 134°. By employing the Schotten-Baumann method for the benzoylation of *n*-benzylsalicylaldoxime, dibenzoyl-β-benzylhydroxylamine (see this vol., i, 24) and salicylaldehyde are obtained. *Acetylbenzylsalicylamide*, OAc·C₆H₄·CO·NH·CH₂Ph, is obtained by acetylating *n*-benzylsalicylaldoxime; it melts at 102°, and gives benzylsalicylamide when treated with sodium ethoxide. A. R. L.

Stereoisomerism of the Benzhydroxamic acids. By W. LOSSEN (*Ber.*, **26**, 2602—2603).—A contribution to the discussion with Hantzsch and Werner (Abstr., 1893, i, 710).

Diphenylmaleïc Anhydride. By G. GYSAE (*Ber.*, **26**, 2478—2486).—*Ethyldiphenylmaleïmide*, C₁₆H₁₀O₂:NEt, is obtained by heating diphenylmaleïc anhydride with a solution of ethylamine in dilute

alcohol in a sealed tube at 100°. It crystallises in yellow needles, and melts at 108°. *Methyldiphenylmaleïmide*, obtained in a similar way to the ethyl compound, crystallises in bright yellow needles, and melts at 158°.

Diphenylmaleïcparabromanil, $C_{16}H_{10}O_2 \colon NC_6H_4Br$, forms brownish-yellow crystals, and melts at 133°. The author could not obtain the corresponding orthonitro-derivative from orthonitraniline and dimaleïc anhydride.

Paratolyldiphenylmaleïmide, $C_{16}H_{10}O_2 \colon NC_7H_7$, forms beautiful brown crystals, and melts at 192°. *β-Napththyldiphenylmaleïmide*, prepared by heating the anhydride, β-naphthylamine, and alcohol at 180°, forms yellowish-grey crystals, and melts at 192°. *Ethylenedidiphenylmaleïmide*, $(C_{16}H_{10}O_2 \colon N)_2C_2H_4$, obtained by heating the anhydride, ethylenediamine, and alcohol at 100°, crystallises in small, bright-yellow plates, melts above 270°, and is extremely insoluble in the ordinary solvents. *Metaphenylenedidiphenylmaleïmide* $(C_{16}H_{10}O_2 \colon N)_2C_6H_4$, is a yellow, crystalline powder, melts at 236°, and is very insoluble.

Piperidodiphenylmaleïc piperidine,

$$C_5NH_{10} \colon CO \cdot C_{14}H_{10} \cdot COOH, C_5NH_{11},$$
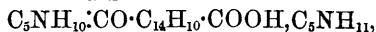
is obtained by heating the anhydride with piperidine and alcohol at 100°; it crystallises in white tufts, and melts at 185—186°. When warmed with acetic acid, hydrochloric acid, or sodium hydroxide, it is decomposed into the anhydride and piperidine. Contrary to the statement of Gabriel and Cohn (Abstr., 1892, 178), the author did not obtain a colouring matter from diphenylmaleïc anhydride and quinaldine. When the two latter compounds are heated together with a trace of sodium acetate at 200°, a compound of the formula $C_{36}H_{28}N_2O_3$ is obtained; it crystallises from alcohol in beautiful yellow needles, melts at 153°, and has no tinctorial properties.

Metaxylaldiphenylmaleïde, $\begin{matrix} CPh \colon CPh \\ | \\ CO\text{---}O \end{matrix} \!\!> C \colon CH \cdot C_7H_7$, is obtained by heating diphenylmaleïc anhydride, metatolylacetic acid, and anhydrous sodium acetate first at 160—180°, and, finally, at 250°. It is an intensely yellow, crystalline powder, and melts at 134°.

Metaxylaldiphenylmaleïmidine, $\begin{matrix} CPh \colon CPh \\ | \\ CO\text{---}NH \end{matrix} \!\!> C \colon CH \cdot C_7H_7$, is obtained by heating the preceding compound with alcoholic ammonia at 100°; it crystallises in long, bright yellow needles, and melts at 224—225°. The above maleïde also yields a similar compound with ethylamine; it crystallises in slender, pale yellow needles.

Metanitro-xylaldiphenylmaleïde, $\begin{matrix} CPh \colon CPh \\ | \\ CO\text{---}O \end{matrix} \!\!> C \colon C(NO_2) \cdot C_7H_7$, is obtained by treating metaxylaldiphenylmaleïde suspended in benzene with a brisk current of nitrous acid (prepared from arsenic trioxide and nitric acid). The solution is allowed to evaporate spontaneously and the product crystallised from a large quantity of cold alcohol. It crystallises in beautiful green tufts, and melts at 165°. When heated in a test-tube, it explodes, the characteristic odour of an isocyanate is observed, and the residue consists of diphenylmaleïc

anhydride. The crude substance, which begins to decompose at 110°, partially decomposes when heated with alcohol, with the formation of diphenylmaleic anhydride.

The author was unable to obtain a nitro-compound from metaxylaï-diphenylmaleïmidine, for oxidation at once takes place, and diphenylmaleïnimide is formed.

The author has further examined the behaviour of isatin towards phenylacetic acid, and finds that water is eliminated with the formation of a compound of the formula $N\diagdown^{C_6H_4-}_{C(OH)}\diagup C{:}CPh{\cdot}COOH$, which may be named *isaphenic acid*. It is obtained by heating isatin, phenylacetic acid, and anhydrous sodium acetate at 200—220°. It crystallises in white leaflets, melts at 294—296°, is easily soluble in ammonia, dilute sodium hydroxide, and sodium carbonate, and forms well-crystallised lead, ammonium, and silver salts. The *monobromo-derivative*, obtained by treating it with bromine in acetic acid solution, melts above 310°. A *monochloro-derivative* is obtained by warming it with phosphorus trichloride and pentachloride. It crystallises in white leaflets, and melts at 220°.

Hydroisophenic acid, $N\diagdown^{C_6H_4-}_{C(OH)}\diagup CH{\cdot}CH{\cdot}COOH$, is obtained by reducing the acid dissolved in dilute sodium hydroxide with 4 per cent. sodium amalgam. It crystallises in small, white leaflets, melts at 202°, and gives a *silver salt* which separates in white flocks.

E. C. R.

Oxidation products of some Aromatic Thiourethanes. By P. JACOBSON and J. KLEIN (*Ber.*, **26**, 2363—2372).—It was shown some time ago (Abstr., 1886, 700, 876) that phenylthiourethane, when oxidised with alkaline ferricyanide in the cold, yields a bisulphide; when heat is applied. and excess of the oxidising agent used, a thioanhydride is formed. It is now found that, in an analogous fashion, β-naphthylthiourethane yields the *ethyl ether* of a *carbamidothionaphthol*, heat being absorbed in the reaction; and para-bromophenylthiourethane, in the cold, yields a bisulphide. Para-nitrophenylthiourethane, however, behaves quite differently, and yields paranitrophenylurethane, sulphur being simply replaced by oxygen.

Phenylthiourethane may be readily reduced to bisulphide by treatment with warm alcoholic hydrogen sulphide; hydrogen chloride converts it, in benzene solution, into phenylic cyanate, ethylic chloride, sulphur, and hydrogen sulphide; the last is not evolved, but reduces more thiourethane to bisulphide.

Carbamidothionaphthol ethyl ether, $C_{10}H_6\diagdown^{N}_{S}\diagup C{\cdot}OEt$, crystallises in yellowish plates, melting at 78—79°; concentrated hydrochloric acid converts it into *carbamidothionaphthol*, which crystallises in white needles, melts at 235—236°, and yields a *sodium* derivative as nacreous plates. When carbamidothionaphthol is heated with alcoholic potash, and air is aspirated through the mixture, *diamido-dinaphthyl bisulphide*, $S_2(C_{10}H_6{\cdot}NH_2)_2$, separates in yellowish flakes; its *hydrochloride*, $C_{20}H_{16}N_2S_2,HCl$, crystallises in bundles of dark yellow, silky needles.

Paranitrophenylthiourethane is best prepared by the action of thiocarbonyl chloride on paranitraniline ; *paranitrophenylthiocarbimide* is formed as an intermediate product, and crystallises in pale yellow needles melting at 112—113°.

Parabromophenylthiourethane bisulphide, $S_2[C(OEt)\!:\!N\cdot C_6H_4Br]_2$, crystallises in colourless needles, melting at 86—87°.   C. F. B.

Ketones from Acrylic acid. By C. MOUREU (*Bull. Soc. Chim.*, [3], **9**, 568—576).—Destructive distillation of calcium acrylate, either alone or mixed with calcium formate, and the action of zinc ethide on acrylic chloride, yield no definite results.

Phenyl vinyl ketone, $COPh\cdot CH\!:\!CH_2$, can, however, be obtained by allowing a solution of acrylic chloride in benzene to fall drop by drop into a mixture of aluminium chloride and carbon bisulphide, and separating the products in the usual way by fractional distillation and treatment with sodium hydrogen sulphite. It is very volatile in steam, and crystallises from the aqueous distillate in long needles melting at 42°. It has a persistent aromatic odour, recalling that of cinnamaldehyde, is slightly soluble in water, and dissolves in alcohol, ether, and chloroform. Phenyl vinyl ketone is the simplest of the unsaturated ketones of the benzene series. It combines directly with the theoretical quantity of bromine, but some substitution takes place at the same time. It differs from the saturated ketones of the benzene series in its property of forming a crystalline compound with sodium hydrogen sulphite, but this property is probably connected with the existence of the double bond. With phenylhydrazine, it yields a well-crystallised but very unstable hydrazone, which melts at 130°.

Paraxylyl vinyl ketone, $C_6H_3Me_2\cdot CO\cdot CH\!:\!CH_2$, is obtained in a similar manner by the action of a solution of acrylic chloride in paraxylene on a mixture of aluminium chloride and carbon bisulphide. It boils between 180° and 240° under a pressure of 30 mm., and usually crystallises in the condensing tube. It is insoluble in water, but dissolves in alcohol and ether, and crystallises from the former in slender, brilliant, silky needles melting at 77—78°. Although an unsaturated compound, it combines extremely slowly with sodium hydrogen sulphite. With phenylhydrazine, it yields a hydrazone which crystallises from alcohol, melts at 132—133°, and is very unstable.

Paraxylylethyl paraxylyl ketone, $C_6H_3Me_2\cdot CO\cdot CH_2\cdot CH_2\cdot C_6H_3Me_2$, is formed together with the preceding compound, and in considerably larger proportion. It boils between 255° and 265° under a pressure of 30 mm., and crystallises from alcohol of 80° in slender, brilliant, white needles melting at 52°. It is insoluble in water, but dissolves in alcohol, ether, and benzene. Its molecular weight, as determined by the cryometric method, is 252 (calc. 266). It is a saturated compound, and, with hydroxylamine, yields a well-crystallised oxime, which crystallises from alcohol of 60° in white needles melting at 82—84°.

The formation of paraxylylethyl paraxylyl ketone may be due to the following changes. A portion of the hydrogen chloride, instead of being liberated, unites with the paraxylyl vinyl ketone to form a

compound, such as $C_6H_3Me_2\cdot CO\cdot CH_2\cdot CH_2Cl$, and the latter acts on the excess of paraxylene after the manner of ordinary alkyl chlorides.

C. H. B.

1 : 3-Diketones. By J. U. NEF (*Annalen*, **277**, 59—78).—The author has shown in his researches on ethylic acetoacetate (Abstr., 1892, 140 ; 1893, i, 628) that the ethereal salts of β-ketonic acids contain the hydroxyl group, and the following experiments furnish evidence that this is also true of the 1 : 3-diketones (compare, however, Claisen, next abstract).

When sodium benzoylacetone is suspended in ether and treated with acetic chloride, the chief product is a neutral compound, *α-benzoyl-β-acetoxypropylene*, $CHBz\ddot{:}CMe\cdot OAc$, which boils at 170° (22 mm.) with partial decomposition, and appears to undergo previous conversion into a stereo-isomeride. The other products are *α-acetylbenzoyl-β-hydroxypropylene*, $CAcBz\ddot{:}CMe\cdot OH$, and benzoylacetone ; they are separated by fractional treatment with alkali, the former being much more strongly acidic than the latter. It melts at 35°, boils at 167° (22 mm.), and forms a *copper* salt which crystallises from benzene in greenish-blue needles, and melts at 228° with decomposition. A certain quantity of α-benzoyl-β-acetoxypropylene is formed by heating benzoylacetone with acetic anhydride at 170°, showing that the latter may be regarded as α-benzoyl-β-hydroxypropylene.

By treating sodium benzoylacetone with benzoic chloride there is formed α-dibenzoyl-β-hydroxypropylene, $CBz_2\ddot{:}CMe\cdot OH$ (Smith, *Inaug. Diss.*, 1889), melting at 115°, together with *α-benzoyl-β-benzoxypropylene*, $CHBz\ddot{:}CMe\cdot OBz$, a neutral oily compound.

When sodium acetylacetone is treated with benzoic chloride, two acidic compounds, namely, acetylacetone and α-acetyl-β-hydroxypropylene, are formed, and two neutral compounds, namely, *α-acetylbenzoyl-β-benzoylpropylene*, $CAcBz\ddot{:}CMe\cdot OBz$, melting at 103°, and an oil, perhaps, $CHAc\ddot{:}CMe\cdot OBz$.

α-Diacetyl-β-hydroxypropylene, $CAc_2\ddot{:}CMe\cdot OH$, an acidic compound boiling at 104° (19 mm.), is obtained, together with a neutral substance, by treating sodium acetylacetone with acetic chloride.

Dry silver acetylacetone reacts with ethylic iodide, forming α-ethylacetylacetone, $CEtAc\ddot{:}CMe\cdot OH$ (Combes, *Ann. Chim. Phys.*, [6], 12, 247), and a neutral *compound*, $CHAc\ddot{:}CMe\cdot OEt$, which boils at 175—180°. A. R. L.

1 : 3-Diketones. By L. CLAISEN and others (*Annalen*, **277**, 162—206 ; compare Nef, preceding abstract).—The author criticises Nef's views on the constitution of ethylic acetoacetate, and also the nomenclature employed by the latter. He thinks that the constitution of the ethylic salt itself and of its metallic derivatives are distinct problems. The conversion of so small a quantity as one-tenth of ethylic acetoacetate, by treatment with acetic anhydride, into an acetyl derivative (Nef), is an argument against rather than in favour of the hydroxyl formula.

The constitution of ethylic diacetoacetate (ethylic acetylacetonecarboxylate), from acetic chloride and ethylic sodacetoacetate,

has been determined by Perkin (Trans., 1892, 823, 854). Its alcoholic solution gives a dark red coloration with ferric chloride; the *copper* salt, $(C_8H_{11}O_4)_2Cu + 2H_2O$, melts at 151°. When ethylic diacetoacetate is heated with hydroxylamine hydrochloride, it gives *ethylic αγ-dimethylisooxazole-β-carboxylate*, $COOEt{:}C{<}^{CMe{:}N}_{CMe{\cdot}O}{\,}^{|}$, which boils at 218—220°; the corresponding *acid* melts at 142°. *Methylic diacetoacetate* melts at 22—23°, and boils at 196—198°.

Ethylic acetylacetone carbonate, $CHAc{:}CMeO{\cdot}COOEt$, is obtained together with ethylic acetylacetonecarboxylate by treating an alkali (preferably the potassium) derivative of acetylacetone with ethylic chlorocarbonate; it is a colourless oil, boils at 124—126° (18 mm.), or at 221—224° (ordinary pressure), with partial decomposition; its sp. gr. is 1·082 at 15°.

When the alkali derivatives of benzoylacetone are suspended in ether and treated with benzoic chloride, benzoylacetone, *dibenzoylacetone*, $C_{17}H_{14}O_3$, and *tribenzoylacetone* are formed. The dibenzoylacetone is strongly acid, and is extracted from the product by sodium carbonate solution; it melts at 101—102°, and gives a blue precipitate with copper acetate solution. The *ferric* salt, $(C_{17}H_{13}O_3)_3Fe + 3H_2O$, is a yellowish-red, crystalline powder. When heated with aqueous alkalis, the dibenzoylacetone decomposes into dibenzoylmethane (m. p. 80—81°) and acetic acid; and if it is dissolved in hot alcohol and allowed to slowly crystallise, an *isomeride* is obtained which melts, when rapidly heated, at 109—112°, and gives no precipitate with copper acetate solution.

Benzoic chloride reacts with the alkali derivatives of acetylacetone forming acetylbenzoylacetone, $CHAc_2Bz$, which melts at 34—35°, and forms a *copper* salt, melting at 224—225°; and dibenzoylacetylacetone, $CAcBz{:}CMe{\cdot}OBz$, melting at 102—103°.   A. R. L.

Nitration of Orthoiodobenzoic and Orthoiodosobenzoic acids. By H. GÜMBEL (*Ber.*, **26**, 2473—2475).—Iodosobenzoic acid is obtained by the action of a mixture of fuming nitric acid (1 part) and concentrated sulphuric acid (3 parts) on orthoiodobenzoic acid at ordinary temperatures. If, however, orthoiodobenzoic acid is heated with 20 times its weight of the acid mixture at 170—175° for 4—5 hours, it yields an *acid* of the formula $NO_2{\cdot}C_6H_3I{\cdot}COOH$, which crystallises in long, lustrous, colourless needles, and melts at 192° (uncorr.). When the iodobenzoic acid is heated with the acid mixture at 135—140° for three hours, it yields *the acid* $NO_2{\cdot}C_6H_3(IO){\cdot}COOH$, which crystallises in slender, white needles, and decomposes about 194—196°. When treated with potassium iodide, it is completely converted into nitro-orthoiodobenzoic acid, and conversely it may be obtained from the latter by oxidation with potassium permanganate.

When orthoiodobenzoic acid is heated with the acid mixture at 220—230°, iodine vapours are formed, but no definite compounds could be isolated.   E. C. R.

Condensation of Aromatic Aldehydes with Cyanacetic acid. By E. FIQUET (*Ann. Chim. Phys.*, [6], **29**, 433—504).—Cyanacetic

acid is best prepared by gradually adding pulverised potassium cyanide to a solution of chloracetic acid in water (2 parts) heated on a water bath, and treating the product cautiously at 0° with hydrochloric acid; the author is unable to verify the melting point (80°) recorded by Van't Hoff, but finds that the acid melts at 69—70°.

Aromatic aldehydes react with cyanacetic acid, forming compounds of the type CHR':C(CN)·COOH, R' being an aromatic alkyl. The production of α-cyanocinnamic acid from benzaldehyde and cyanacetic acid has already been described (Abstr., 1892, 1340); this acid, if heated with aqueous potash, decomposes into malonic and benzoic acids, whilst if heated with water at 170—180°, benzaldehyde and cyanacetic acid are regenerated. The *sodium, silver,* and *copper* salts are described; the *methylic* salt crystallises in clinorhombic, tabular prisms, $a : b : c = 1·5023 : 1 : 2·3610$; angle of prism = 98° 37′ The ethylic and other salts have been described by Carrick (Abstr., 1892, 1086). If the ethylic salt is treated with gaseous ammonia in alcoholic solution, a crystalline *compound*,

$$CHPh:C(CN)·COOEt,CHPh:C(CN)·CONH_2,$$
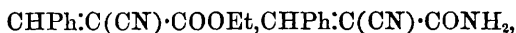
is formed, which melts at 187°, and decomposes into benzaldehyde and ammonium malonate when heated with water at 180—200°; it is, therefore, isomeric with the compound described by Carrick (*loc. cit.*). Paranitrobenzoic acid is formed by treating α-cyanocinnamic acid with fuming nitric acid. Continued heating of α-cyanocinnamic acid on the water bath with phosphorus pentachloride gives rise to the formation of *benzylideneacetic chloride,* a compound which is converted by water into α-cyanocinnamic acid, and by alcohol into the ethylic salt of the same acid. Cinnamonitrile, obtained by heating α-cyanocinnamic acid above its melting point, boils at 254—256°, and its sp. gr. at 0°/0° is 1·037. If the nitrile is boiled with hydrochloric acid or potash, cinnamic acid is formed, and, when it is treated with hydrogen sulphide in alcoholic solution, it yields a yellow, crystalline *compound,* $C_9H_7S·NH_2$, melting at 112°; it combines with bromine, forming *phenyldibromopropionitrile,* which decomposes when distilled.

The three toluic aldehydes were prepared by a modification of Étard's method, which is described. *Metamethyl-α-cyanocinnamic acid,* $C_6H_4Me·CH:C(CN)·COOH$, obtained by heating metatoluic aldehyde with cyanacetic acid at 150—160°, is a white, crystalline compound, melts at 156°, is insoluble in water, and devoid of odour; when heated with potash, metatoluic acid is formed. The *methylic* salt melts at 95°, and the *ethylic* salt at 85°. *Metamethylcinnamonitrile* passes over at 170°, when the last described acid is distilled under a pressure of 30 mm.; it has an aromatic odour, its sp. gr. at 0°/0° is 1·038, and it is converted into metamethylcinnamic acid when heated on the water bath with potash.

Paramethyl-α-cyanocinnamic acid, from paratoluic aldehyde, melts at 214°, and is less soluble in alcohol and benzene than the last described isomeride; the *methylic* salt melts at 110—112°, and the *ethylic* salt at 94°. When the acid is distilled under diminished pressure, *paramethylcinnamonitrile* passes over; it is a crystalline solid, melts at 79—80°, and gives paramethylcinnamic acid when heated with

potash. *Orthomethyl-α-cyanocinnamic acid* melts at 202°, the *methylic* salt at 89—90°, and the *ethylic* salt at 60°. When the acid is distilled, it decomposes into a compound which yields orthomethylcinnamic acid on treatment with potash.

Paranitro-α-cyanocinnamic acid, $NO_2 \cdot C_6H_4 \cdot CH\!:\!C(CN) \cdot COOH$, is obtained by heating paranitrobenzaldehyde with cyanacetic acid at 160—170°; it forms white laminæ, and melts at 208°; the *ethylic* salt melts at 169—170°. *Orthonitro-α-cyanocinnamic acid* melts at 226—228°, and *metanitro-α-cyanocinnamic acid* at 214—216°.

Cinnamyl-α-cyanoacrylic acid, $CHPh\!:\!CH \cdot CH\!:\!C(CN) \cdot COOH$, obtained by heating cinnamaldehyde with cyanacetic acid, forms small, yellow crystals, and melts at 212°; it yields cinnamic acid when treated with potash, and paranitrobenzoic acid on treatment with fuming nitric acid. The *silver* and *calcium* salts are both amorphous; the *methylic* salt melts at 145°, and the *ethylic* salt at 118—120°. *Cinnamylacrylonitrile* passes over at 159°, when the acid is distilled under a pressure of 285 mm.; it is a colourless liquid of sp. gr. 0°/0° = 1·037, having an odour resembling that of cinnamonitrile, and combines with four equivalents of bromine. When the nitrile is heated with potash, *cinnamylacrylic acid* melting at 165—166° is formed. A. R. L.

Dry Distillation of Calcium Veratrate. By W. HEINISCH

(*Monatsh.*, **14**, 455—461).—The distillate contains methylic veratrate and veratrol together with small quantities of guaiacol and veratric acid; the residue contains a small quantity of catechol. These results should be compared with those obtained by other observers in the case of calcium anisate (Abstr., 1882, 616) and dimethyl-α-resorcylate (Abstr., 1888, 148). C. F. B.

Synthesis of β-Pipecoline and Preparation of δ-Valerolactone. By R. FUNK

(*Ber.*, **26**, 2568—2576).—The method employed by Gabriel (Abstr., 1892, 717) for the synthesis of piperidine is applied by the author to the synthetical production of β-pipecoline. *Ethylic γ-phenoxypropylisosuccinate*, $OPh \cdot C_3H_6 \cdot CMe(COOEt)_2$, may be prepared by the action of γ-chloropropylic phenylic ether on ethylic sodio-isosuccinate, or by that of methylic iodide on ethylic sodio-γ-phenoxypropylmalonate; it boils at 268—270° under 130 mm. pressure. *Ethylic γ-phenoxypropylmalonate* can only be distilled without decomposition under diminished pressure; it boils at 265—266° under 140 mm. pressure; it forms large, rhombic tablets which melt at 32°. *γ-Phenoxypropylisosuccinic acid*, obtained by hydrolysis of the ethylic salt, crystallises from water in colourless plates, and melts with decomposition at 118°. The *silver salt* forms microscopic needles. When the acid is heated, carbonic anhydride is evolved, and *α-methyl-δ-phenoxyvaleric acid*, $OPh \cdot C_3H_6 \cdot CHMe \cdot COOH$, formed; this distils at 327°, and, when cooled, solidifies in crystals which melt at 36°, and are very soluble in alcohol and other solvents. The *nitrile* of this acid is prepared by the distillation of the acid with lead thiocyanate, and is a yellow oil, which boils at about 300°. The reduction of the nitrile by the action of sodium on its alcoholic solution yields *β-methyl-ε-phenoxyamylamine*, $OPh \cdot C_3H_6 \cdot CHMe \cdot CH_2 \cdot NH_2$, as an oil

which absorbs carbonic anhydride from the air with great rapidity. The *hydrochloride* forms small, hygroscopic needles, and melts at 88°; the *picrate* melts at 106—110°, and the *platinochloride* crystallises in yellow needles. When the base is heated with fuming hydrochloric acid at 180°, it is converted into the very hygroscopic *hydrochloride* of *β-methyl-ε-chloramylamine*, $CH_2Cl\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot NH_2$. The *picrate* of this base crystallises from water in small needles melting at 65—66°, and the *platinochloride* forms sparingly-soluble small, yellow plates. When the hydrochloride is heated with aqueous potash, β-pipecoline (β-methylpiperidine) is formed. The base thus obtained is identical with that prepared by Hesekiel (*Ber.*, 18, 910).

Henry (*Bull. Soc. Chim.*, 45, 341) has shown that γ-chlorobutyric acid loses hydrogen chloride when distilled, butyrolactone being produced. In order to ascertain whether δ-*chlorovaleric acid* behaves in a similar manner, the author prepared this substance by heating δ-phenoxyvaleric acid (Gabriel, Abstr., 1892, 717) with fuming hydrochloric acid at 180°. The acid forms a brown oil, which solidifies in a freezing mixture, and melts at about 4°. When it is boiled in a flask, hydrogen chloride is evolved and δ-*valerolactone*,

$$O<^{CH_2\cdot CH_2}_{CO\cdot CH_2}>CH_2,$$
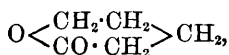
is formed as a liquid boiling under the atmospheric pressure at about 230°. It is soluble in water, alcohol, and ether, and, when treated with alkalis, yields salts of the hydroxy-acid.

The compound obtained by Weidel (Abstr., 1891, 733). which he terms δ-valerolactone, is different from this substance, since it boils at 222—226° at a pressure of 56 mm. A. H.

Derivatives of Triacetylgallic acid. By H. Schiff (*Annalen*, 277, 206—208).—The melting point of triacetylgallanilide was erroneously printed 101—102° in a former paper (Abstr., 1893, i, 167); it should be 161—162°, as since shown by Cazeneuve. Triacetylgallacetamide melts at 163°, as stated by Marx (Abstr., 1891, 1220). A. R. L.

Ethylic Opianate. By R. Wegscheider (*Monatsh.*, 14, 311—314; compare Abstr., 1892, 1208).—The ethylic opianate melting at 92°, already known, is a pseudo-salt. The normal salt may be prepared by the action of ethylic iodide on silver opianate and of ethylic alcohol on opianic chloride. The new salt is readily soluble in alcohol, &c., sparingly in water, and does not easily crystallise. It melts at 63·5—64·5°. Both this salt and the normal methylic salt are distinguished from the corresponding pseudo-salts by the fact that they are exceedingly difficult to burn in a combustion tube (compare Claisen, *Ber.*, 25, 1768). A. H.

Dependence of Chemical Reaction on the Presence of Water. By R. Otto (*Ber.*, 26, 2050—2053).—In connection with Baker's recent work on the influence of water on chemical changes (Proc., 1893, 129), the author observes that a number of organic substances, such as benzenesulphonic chloride, phenylic disulphoxide, phenylic bisulphide, paratoluenesulphonic chloride, and benzenesulph-

d 2

inic acid, whilst readily reduced by nascent hydrogen in presence of water, are not attacked if water be excluded.   W. J. P.

Action of Sulphurous Anhydride on Sodium Phenoxide. By C. SCHALL (*J. pr. Chem.*, [2], **48**, 241—253).—When sulphurous anhydride is passed over sodium phenoxide at the ordinary temperature, the product is not the analogue of Kolbe's sodium phenylcarbonate, but the phenyl salt of sodiumsulphonic acid.

Phenylic sodiumsulphonate, $NaSO_2 \cdot OPh$, is a yellowish-white, light, hygroscopic powder; it is almost insoluble in alcohol, and is slowly decomposed by water with formation of phenol and sodium hydrogen sulphite. When heated with methylic iodide under pressure, it yields *phenylic methanesulphonate*, $CH_3 \cdot SO_2 \cdot OPh$, together with some anisoïl. This crystallises in laminæ or needles, melts at 61—62°, boils at 279° (uncorr.), and may be sublimed; it dissolves sparingly in cold light petroleum and in water, but freely in other solvents, including strong sulphuric acid.

Parabromophenylic methanesulphonate, $CH_3 \cdot SO_2 \cdot OC_6H_4Br$, obtained by brominating the phenylic salt, crystallises in prisms, and melts at 83°; it dissolves freely in ether, benzene, and chloroform, but sparingly in alcohol; it is volatile with steam. By hydrolysis, it yields parabromophenol. The corresponding *tetrabromo*-derivative (probably $Br_4 = 2 : 3 : 4 : 5$) is prepared by heating the bromo-derivative with bromine and fused aluminium bromide; it crystallises in white, silky needles, melts at 164—165°, and dissolves freely in cold benzene and in warm alcohol and carbon bisulphide; the tetrabromophenol which it yields on hydrolysis melts at 128—129°. By increasing the proportion of bromine and aluminium bromide, the *pentabromo*-derivative is obtained; this crystallises in white needles, and melts at 171°.

Paranitrophenylic methanesulphonate, $CH_3 \cdot SO_2 \cdot OC_6H_4 \cdot NO_2$, is the product of the nitration of phenylic methanesulphonate; it melts at 94—95°, and dissolves in ether, alcohol, benzene, and glacial acetic acid. The corresponding *amido*-derivative crystallises in white needles, melts at 89—90°, and dissolves in alcohol and in ether. The *acetamido*-derivative crystallises in needles, and melts at 177—178.°

Dinitrophenylic methanesulphonate $[(NO_2)_2 = 2 : 4]$ is formed when the nitration of the phenylic salt is conducted with an excess of nitric acid; it crystallises in laminæ, and melts at 82—84°. The corresponding *diamido*-derivative forms needles which melt with slight blackening at 103—104°, and dissolve in warm benzene, chloroform, and alcohol. The *diacetyldiamido*-derivative forms felted needles, and melts with slight blackening at 236—237°.

Phenylic ethanesulphonate, $CH_2Me \cdot SO_2 \cdot OPh$, is obtained, together with some phenetoïl, when phenylic sodiumsulphonate is heated with ethylic iodide; it crystallises in white laminæ, melts at 34—35°, boils at 287—288°, and dissolves easily in benzene and in alcohol. Hydrolysis converts it into ethanesulphonic acid and phenol.

Phenylic α-propanesulphonate, $CH_2Et \cdot SO_2 \cdot OPh$, from phenylic sodiumsulphonate and α-propylic iodide, is a brown, uncrystallisable, sparingly soluble, viscid oil.

Paracresylic sodiumsulphonate, $NaSO_2 \cdot OC_6H_4Me$, is prepared from sodium paracresoxide in a manner similar to that described above for the preparation of the phenylic compound. *Paracresylic methanesulphonate* crystallises in white cubes, melts at 44·5—46°, and boils with slight decomposition at 295° (uncorr.), and undecomposed at 260—264° under a pressure of 207 mm.; it is volatile with steam, and sublimes; alcohol dissolves it freely; oxidation converts it into *paracarboxylphenylic methanesulphonate*, $CH_3SO_2 \cdot O \cdot C_6H_4 \cdot COOH$, which forms white needles, melts at 224°, and dissolves freely in ether and warm alcohol.

α- and β-*Naphthylic sodiumsulphonates*, $NaSO_2 \cdot OC_{10}H_7$, were also prepared.   A. G. B.

Action of Phosphorus Pentachloride on Benzoicsulphinide. By I. REMSEN (*Ber.*, **26**, 2634—2635).—The author points out that Jesurin (Abstr., 1893, i, 715) has overlooked the work of Remsen and Dohme (Abstr., 1889, 992), which contains much of the matter published as new by Jesurin. In conjunction with certain of his students, the author has found that the chloride of benzoicsulphinide consists of two isomeric compounds of melting points 78° and 22° respectively; both are converted by ammonia into benzoic sulphinide. A full description of these and other experiments with parachlorocyanobenzene will appear later in the *American Chemical Journal*.
                                                                    A. R. L.

Intramolecular Change of Phthalides into Derivatives of α γ-**Diketohydrindene.** By F. NATHANSON (*Ber.*, **26**, 2576—2582; compare Abstr., 1893, i, 346).—When a solution of sodium in methylic alcohol is added to one of benzalphthalide,

$$CO <_{-O-}^{C_6H_4} > C{:}CHPh,$$
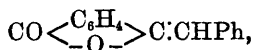
in the same solvent, the colourless liquid becomes dark red, and a mass of crystals separates, consisting of the sodium compound of β-*phenyl-*α γ-*diketohydrindene*, $C_6H_4 \cdot (CO)_2 \cdot CHPh$. The same result is obtained when ethylic alcohol is used, but if even a small amount of water is present, the yield is no longer quantitative, and deoxybenzoincarboxylic acid, $COOH \cdot C_6H_4 \cdot CO \cdot CH_2Ph$, is produced. Phenyldiketohydrindene is also formed when benzalphthalide is boiled with alcoholic potash, or when the methylic salt of deoxybenzoincarboxylic acid is hydrolysed with alcoholic potash. Phenyldiketohydrindene crystallises in white, nacreous plates melting at 145°. It is insoluble in water, but dissolves readily in other solvents, forming yellow or red solutions; it yields a blue solution with concentrated sulphuric acid; it is a strong acid, and forms a number of coloured salts. Attempts to reduce it to phenylhydrindene proved unsuccessful. *Phenyldiketohydrindenephenylhydrazone* crystallises in fine, yellow, matted needles melting at 170—174°. The *dioxime* forms small, white needles melting at 193—196°. *Phenylmethyldiketohydrindene*, $C_6H_4 \cdot (CO)_2 \cdot CMePh$, is prepared by the action of methylic iodide on the sodium compound, and forms colourless, cubic crystals

melting at 154—155°. The corresponding *ethyl* compound melts at 103—105°.

Ethylic phenyldiketohydrindeneacetate, $C_6H_4\text{:}(CO)_2\text{:}CPh\cdot CH_2\cdot COOEt$, is obtained by the action of ethylic chloracetate on the sodium compound, and melts at 104°. *Phenylbromodiketchydrindene,*

$$C_6H_4\text{:}(CO)_2\text{:}CPhBr,$$
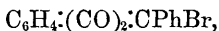
is obtained by the direct action of bromine, and crystallises from benzene in white needles melting at 105°. It has no acid properties. The *chloro*-derivative is formed by treating the diketo-compound with phosphorus pentachloride, and crystallises in yellow needles melting at 114—116°. The halogen atom of these compounds is not removed by boiling with alcoholic ammonia or potassium cyanide, but readily reacts with aniline, forming an *anilido*-derivative, $C_6H_4\text{:}(CO)_2\text{:}CPh\cdot NHPh$, which melts at 210—211°. *Bisphenyldiketohydrindene,* $C_6H_4\text{:}(CO)_2\text{:}CPh\cdot CPh\text{:}(CO)_2\text{:}C_6H_4$, is produced by the oxidation of the diketohydrindene by means of nitrous acid. It crystallises in white, lancet-shaped needles melting at 208°. *Dinitrophenyldiketohydrindene* is obtained by the direct action of fuming nitric acid, and melts at 128—131°.

Ethylidenephthalide, when treated with sodium methoxide, is converted into β-methyldiketohydrindene, identical with that described by Wislicenus (Abstr., 1889, 1067).

Ethinediphthalide is converted in a similar manner into *bisdiketohydrindene,* $C_6H_4\text{:}(CO)_2\text{:}CH\cdot CH\text{:}(CO)_2\text{:}C_6H_4$; this crystallises from hot nitrobenzene in long, violet needles which do not melt below 350°. It is insoluble in solvents of low boiling point, but dissolves in alkalis, forming violet solutions from which it is precipitated unchanged by acids.　　　　　A. H.

Diphenyl Group. By R. LOEWENHERZ (*Ber.,* **26**, 2486—2487).—The diphenyltetracarboxylic acid obtained by the author (Abstr., 1892, 1464) by the oxidation of ditolyldicarboxylic acid with potassium permanganate corresponds with phthalic acid, and the author therefore names it *diphthalic acid.* It is less soluble in water than phthalic acid, crystallises in colourless needles, and does not melt at 250°. When heated with resorcinol, it yields a *difluorescein,* which is very similar to fluorescein, exhibits a somewhat stronger fluorescence, and is converted by bromine into a *dieosin.* The latter closely resembles eosin, and gives almost the same shades on wool.

A *dihelianthin* is obtained by combining diazotised benzidinedisulphonic acid with dimethylaniline; it is very similar to dimethylorange. The corresponding *diethyl compound* obtained from benzidinedisulphonic acid and diethylaniline is very similar to diethyl-orange.　　　　　E. C. R.

Alkyl Derivatives of Benzoïn. By E. FISCHER (*Ber.,* **26**, 2412—2415).—When a methyl alcoholic solution of benzoin is saturated with gaseous hydrogen chloride at 30—40°, and then allowed to remain at the ordinary temperature, *methylbenzoin,* $CPhO\cdot CHPh\cdot OMe$, is formed, and may be obtained crystallised in white needles which melt at 49—50° (corr.). It is oxidised by nitric

acid to benzile, yields an oily product with phenylhydrazine, and, with hydroxylamine, yields *methylbenzoïnoxime*, $NOH:CPh·CHPh:OMe$, crystallising in small needles, and melting at 130—132° (uncorr.).

Ethylbenzoïn, $CPhO·CHPh·OEt$, resembles the methyl compound; it melts at 62° (corr.), and yields compounds with phenylhydrazine and hydroxylamine, but they have not been obtained crystallised.

C. F. B.

Anilides of Benzoïn and Benzile. By B. LACHOWICZ (*Monatsh.*, **14**, 279—293).—In this investigation, special care was taken to vary the methods and conditions of preparation, in order to ascertain whether any of the mono- or di-anilides occurred in two isomeric forms; this was in no instance found to be the case.

Benzoïnanil, $NPh:CPh·CHPh·OH$, has been prepared by Voigt (*J. pr. Chem.*, **34**, 2). It combines with 1 mol. of hydrogen chloride to form a *hydrochloride*, which crystallises from hot alcohol in short, colourless needles melting at 185°. *Benzoïnanilanilide*, $NPh:CPh·CHPh·NHPh$, is not formed by the action of aniline on benzoïn even at 240°, but may be obtained when aniline hydrochloride is heated with benzoïn at 160°. It crystallises from alcohol in colourless needles melting at 125°. This substance is not acted on by boiling alcoholic potash or hydrochloric acid, but is converted by nitrous acid into a yellow, unstable nitroso-compound. Benziledianil, $NPh:CPh·CPh:NPh$, which has been previously prepared by Siegfeld (*Ber.*, **25**, 2601), is also formed when benzoïnanil is heated in the air with aniline, the atmospheric oxygen taking part in the reaction. It is decomposed by hydrochloric acid, but not by alcoholic potash. On treatment with phenylhydrazine hydrochloride, it is converted into benzilediphenylhydrazone. *Benzoïnanilparatoluidide*, $NPh:CPh·CHPh·NH·C_7H_7$, is obtained by heating together benzoïnanil and paratoluidine hydrochloride. It forms colourless prisms, and melts at 139°. On repeated recrystallisation from dilute alcohol, it is converted into a mixture of benzoïnanilanilide and benzointoluidiltoluidide. *Benzileanilparatoluidil*, $NPh:CPh·CPh:N·C_7H_7$, is prepared by heating benzoïnanil with paratoluidine in an open vessel, and forms flat, yellow needles melting at 135°. On treatment with hydroxylamine hydrochloride, it yields benzileoximeparatoluidil (Abstr., 1892, 1470). *Benzoïnparatoluidilparatoluidide*, $C_7H_7·N:CPh·CHPh·NH·C_7H_7$, forms long, colourless prisms melting at 155—156°. Benzilediparatoluidil, $C_7H_7·N:CPh·CPh:N·C_7H_7$, previously prepared by Voigt, is also formed when benzoïnparatoluidil is heated with paratoluidine in an open vessel. *Benzoïnparatoluidilanilide*, $C_7H_7·N:CPh·CHPh·NHPh$, forms long, colourless needles melting at 141°. It differs from benzoïnanilparatoluidide, with which it is isomeric, in not being altered by repeated crystallisation. *Benzileparatoluidilanil*, obtained by heating benzileparatoluidil with aniline in an open vessel, is in every respect identical with benzileanilparatoluidil. A. H.

Indoxazen Group. By O. LIST (*Ber.*, **26**, 2451—2457; Abstr., 1893, i, 469).—An examination of the oil obtained by nitrating deoxybenzoïn at 0° (Pictet, *Ber.*, **19**, 1064) shows that it contains about

25—30 per cent. of orthonitrodeoxybenzoïn, together with benzile and benzoïn; the latter compound is obtained in large quantities when the nitration is performed at temperatures above 10°. Orthonitrodeoxybenzoïn crystallises in radiating needles, melts at 73—74°, gives a blue coloration with alcoholic potash, and is completely converted into α-phenylindole when treated with ammonia and zincdust. Its *oxime* crystallises in pale yellow needles, melts at 118°, and gives red solutions with alkalis. Nitrous acid is not eliminated from the molecule either by warming with pure sodium hydroxide, or by heating with sodium ethoxide in a sealed tube.

Paranitrodeoxybenzoïnoxime is prepared from paranitrodeoxybenzoïn, which is also obtained by nitrating deoxybenzoïn. It crystallises in yellowish-brown needles, melts at 105°, and gives a red coloration with alkalis. The author was unable to eliminate the nitrogroup by treatment with alkali.

Orthonitrodeoxybenzoïn dissolved in acetic acid is easily converted into orthonitrobenzile by oxidation with chromic acid. It crystallises in yellow needles, and melts at 98°.

Orthonitrobenzileoxime, $NO_2 \cdot C_6H_4 \cdot C(NOH) \cdot COPh$, crystallises in pale yellow needles or quadratic tablets, melts at 185° with decomposition, and gives yellow solutions with alkalis. When boiled with an aqueous solution of sodium hydroxide, it yields salicylic and benzoic acids, which are formed by the decomposition of an unstable benzoylindoxazen. When boiled with sodium carbonate, salicylonitrile and benzoic acid are produced.

Orthonitrobenziledioxime is obtained by heating the monoxime with hydroxylamine hydrochloride and alcohol in a sealed tube at 120—130°. It crystallises in large, yellowish-white prisms, melts at 244° with decomposition, and gives red solutions with alkalis. When heated with aqueous sodium hydroxide, it yields hydroxylamine, salicylic and benzoic acids, the decomposition products of an unstable indoxazen compound of the formula $\begin{smallmatrix} C_6H_4 \\ O \cdot N \end{smallmatrix}\!\!>\!\!C \cdot PH\!:\!NOH$.

Paranitrobenzile is obtained by oxidising paranitrodeoxybenzoïn with chromic acid, and is identical with the compound obtained by Haussmann by treating benzoïn with nitric acid.

The author once obtained a *second oxime of orthonitrobenzile*, $NO_2 \cdot C_6H_4 \cdot CO \cdot CPh\!:\!NOH$, by working with a strongly alkaline solution. It melts at 265° with decomposition, and does not evolve nitrous acid when treated with sodium hydroxide.

1·4′-*Dinitroanthraquinoneoxime* crystallises in long, rose-red prisms, melts at 253° with a sudden decomposition, and does not lose its nitro-group when heated with concentrated sodium methoxide.

E. C. R.

Hydrocroton. By G. Ciamician and P. Silber (*Ber.*, **26**, 2635—2638).—A polemical paper, being a reply to Hesse (Abstr., 1893, i, 718).

1:4-Amidoacetonaphthalidesulphonic acid. By A. Ammelburg (*J. pr. Chem.*, [2], **48**, 286—292).—This acid (D.P. 66354, 1891) is prepared by sulphonating 1:4-amidoacetonaphthalide. It is a spar-

ingly soluble crystalline powder; a solution of it is coloured brilliantly blue by ferric chloride or chromic acid; its salts with the alkalis and alkaline earths are soluble in water. The *barium* salt crystallises with $7H_2O$; the *potassium* salt is anhydrous; the *zinc* salt crystallises with $3\frac{1}{2}H_2O$, and is freely soluble in water; the *lead* salt crystallises with $1\frac{1}{2}H_2O$, and is sparingly soluble in water.

By oxidising the acid with potassium permanganate, a little phthalic acid is produced; but when fused with potash, it yields β-hydroxyphthalic acid. The latter reaction indicates that the sulphonic group is in a β-position of the ring which does not contain the amido-groups. That this position is 2′ was provisionally settled by diazotising the acid, reducing the product to the hydrazine derivative, and treating this with cupric chloride, whereby a naphthylaminesulphonic acid was produced which corresponded with Erdmann's 1 : 2′-acid, although the difference between the 1 : 2′- and the 1 : 3′-acids is too slight for certainty (compare Erdmann, Abstr., 1893, i, 653).

A. G. B.

Phenonaphthacridone. By M. Schöpff (*Ber.*, **26**, 2589—2598).— The presence of zinc chloride is not essential for the conversion of 2 : 3-anilidonaphthoic acid into phenonaphthacridone, as the change takes place when the former compound, or a mixture of β-hydroxy-naphthoic acid and aniline, is heated alone at 250°. A certain amount of phenonaphthacridone is obtained by heating the anilidonaphthoic acid with hydrochloric acid of 1·03 sp. gr. in a sealed tube at 180°. The most convenient method of preparing large quantities of pheno-naphthacridone consists, however, in heating the anilidonaphthoic acid (250 grams), or a mixture of its components, with zinc-dust (100 grams) for 5—6 hours, in an oil-bath at 200—220°. The product is repeatedly boiled with dilute hydrochloric acid, and subsequently with alkali; it is crystallised from dilute alcohol, whereby the substance melting at about 240° (previously regarded as an isomeride of phenonaphthacridone) is obtained. Treatment of this substance with cold chloroform extracts phenyl-β-naphthylamine (m. p. 108—109°) leaving phenonaphthacridone; the supposed dihydrophenonaphth-acridone obtained by distilling it with zinc-dust (Abstr., 1893, i, 476) is β-dinaphthylamine (m. p. 170·5°). Phenonaphthacridone,

$$C_{10}H_6 <^{CO}_{NH}> C_6H_4,$$
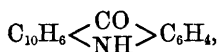
has neither basic nor acidic properties, and is sparingly soluble in most solvents, the solutions exhibiting a greenish fluorescence; it is, however, readily soluble in phenol, and the solution in the latter is devoid of fluorescence; concentrated sulphuric acid dissolves it, forming a deep red solution. It crystallises from alcohol in lustrous, golden-yellow leaflets, and melts at 304—305°. The *ethyl* derivative, $C_{10}H_6 <^{CO}_{NEt}> C_6H_4$, melts at 174—175°; and the *benzyl* derivative at 188—189°. Direct acetylation having been found impossible the author endeavoured to prepare the acetyl derivative by heating 2 : 3-*acetanilidonaphthoic acid*, which melts at 225—227°; under these

circumstances, however, phenonaphthacridone and acetic acid are formed.

Chlorophenonaphthacridine, $C_{10}H_6 <^{CCl}_{N-} > C_6H_4$, is obtained when phenonaphthacridone is heated with a mixture of phosphorus penta-chloride and phosphorus oxychloride at 100—120°; it forms orange-red needles, and melts at 165°.

Phenonaphthacridine, $C_{10}H_6 <^{CH}_{N-} > C_6H_4$, prepared by distilling phenonaphthacridone with zinc-dust, forms white needles, melts at 289°, is sparingly soluble in most solvents, but readily so in chloro-form, the colourless solution having a violet fluorescence. It dissolves in glacial acetic acid, hydrochloric acid, and sulphuric acid, forming intensely red solutions. Its basic properties are feeble.

<div align="right">A. R. L.</div>

α- and *β*-**Naphthaleneindigo.** By H. WICHELHAUS (*Ber.*, **26,** 2547—2550).—The two isomeric forms of naphthaleneindigo can be obtained by melting 24 parts of α- or β-naphthylamine with 16 parts of chloracetic acid and 50 parts of anhydrous sodium acetate, which has been mixed with a little ordinary acetic acid. At about 180°, the mass becomes almost dry, and 50 parts of potash are then added, the temperature being raised to 290°. The product is treated with water, and the insoluble residue washed with hot, dilute hydrochloric acid, and, if necessary, extracted with ether. The crude material thus obtained is then purified by reduction, re-oxidation, and recrys-tallisation from aniline. α-Naphthaleneindigo crystallises from aniline in violet-black needles, whilst the β-compound separates from the same solvent in bluish, indistinct crystals. In the form of powder both isomerides show a distinct cupreous lustre when rubbed. They both sublime in needles with a cupreous lustre, the β-compound with less readiness than the α-derivative. The molecular weight of the α-isomeride was determined by the boiling point method, aniline being employed, and was found to be 464. The solubility of the β-com-pound in aniline was too small to admit of the determination being carried out. The reduction of these indigoes may be effected by means of hyposulphite or grape sugar in the presence of much free alkali, but is best done by warming with ferrous sulphate and potash. The formulæ of these compounds are probably quite analogous to that of ordinary indigo, $C_{10}H_6 <^{NH}_{CO} > C:C <^{NH}_{CO} > C_{10}H_6$ [NH : CO = 1 : 2 in the case of the α-compound, = 2 : 1 in that of the β-compound], but this point has not yet been definitely settled.

The characteristic colorations of ordinary indigo, and α- and β-naphthaleneindigo, are summarised in the following table.

	Ordinary indigo.	α-Naphthalene-indigo.	β-Naphthalene-indigo.
Reduction product in solution	yellow	orange	red.
Vapour	red	violet	blue.
Solution in aniline, chloroform, benzene, acetic acid, &c.	red ; violet to blue	blue	bluish - green to green.
Sulphonic acid in aqueous solution	blue	blue on boiling; bluish-green in the cold	bluish-green.
Sulphonic acid on wool and silk	blue	blue to green	green.
Cotton dyed in vat	blue	blue to green	green.

The sulphonic acids are being further investigated.   A. H.

Colour of Acenaphthylene. By C. GRÄEBE (*Ber.*, **26**, 2354—2355).—The author is unable to obtain acenaphthylene other than coloured, and so regards it, like dibiphenylene-ethane (Abstr., 1893, i, 38), as, in fact, a coloured hydrocarbon. The colour of these two substances, $\dfrac{CH}{CH}{>}C_{10}H_6$ and $\dfrac{C_6H_4}{C_6H_4}{>}C{=}C{<}\dfrac{C_6H_4}{C_6H_4}$, appears to be conditioned by the presence of the group $>C{=}C<$, but also by the nature of the other groups united with it (compare Armstrong, Proc., 1892, 192).   C. F. B.

Terpenes and Ethereal Oils. By O. WALLACH (*Annalen*, **277**, 105—154).—Those terpene and terpinene compounds which are derivatives of paracymene may be distinguished by the position of the double bonds, numbering the carbon atoms in the direction of the hands of a watch from that which carries the methyl group.

Of the three theoretically possible α-keto-dihydroparacymenes, only one, the $\Delta^{3,\,5}$ modification, contains an asymmetrical carbon atom ; inasmuch, therefore, as the only known representative of this series, ordinary carvone, exists in optically active modifications, it must have this constitution. The existence of four α- and four β-ketotetrahydroparacymenes is indicated by theory, and each in optically active forms, so that at least 24 modifications are rendered possible. An even greater number of hydroxy-derivatives (dihydrocarveols) is indicated, as in this case the hydroxyl group may be attached to the carbon atom carrying the alkyl groups ; this is probably so in terpineol. Only two ketohexahydroparacymenes are conceivable ; v. Baeyer has synthesised the α-keto-derivative (Abstr., 1893, i, 359), and the β-keto-derivative is menthone. Four hydroxyhexahydrocymenes are theoretically possible, menthol being 3-hydroxyhexahydrocymene. The geometrical isomerides belonging to the last-mentioned class exhibit great differences in their physical properties, which remark also applies to the amido-derivatives (menthylamines; Abstr., 1893, i, 724).

When the supposed trihydroxyterpene, $C_{10}H_{20}O_3$, obtained by oxid-ising terpineol (Abstr., 1893, i, 596), is heated with dilute sulphuric acid, it yields cymene, and a compound $C_{10}H_{16}O$ (see below). As terpineol appears to be a tertiary alcohol, the hydroxyl groups occupying, probably, the positions 1 or 4, the constitution of the above-mentioned oxidation product may be $1 : 2 : 4$- or $1 : 3 : 4$-tri-hydroxyhexahydrocymene.

When *terpineol dibromide* is digested on the water bath with an excess of moist silver oxide or lead oxide, pinol hydrate, $C_{10}H_{18}O_2$ (m. p. 131°) is obtained. The latter yields pinol when treated with dilute acids. Pinol (sobrerol) is also obtained in good yield when the terpineol bromide is treated with alcoholic potash. The compound $C_{10}H_{16}O$, obtained by oxidising the supposed trihydroxyterpene with chromic acid, is converted into terpenylic acid, $C_8H_{12}O_4$, when heated on the water bath with alkaline permanganate. When either of the compounds $C_{10}H_{20}O_3$, $C_{10}H_{16}O_3$, $C_{10}H_{18}O_4$ (pinolglycol), or terpinylic acid is treated in alkaline solution with bromine, carbon tetrabromide is formed.

Terpineol nitrosochloride, $C_{10}H_{18}O\cdot NOCl$, is obtained by adding ethylic nitrite to a solution of terpineol in glacial acetic acid, cooled in a freezing mixture, and subsequently dropping in hydrochloric acid; it crystallises from methylic alcohol in needles. The *piperidide*, $NO\cdot C_{10}H_{17}(OH)\cdot C_5NH_{10}$, melts at 159—160°, the *anilide* at 155—156°.

The compound $C_{10}H_{16}O$, obtained by heating the supposed trihydr-oxyterpene with dilute sulphuric acid, boils at 231—233°, has a sp. gr. at $20° = 0.929$, and a specific refractive power $[n]_D = 1.48197$. It behaves as a ketone, in that when treated with an excess of hydr-oxylamine hydrochloride, it forms an oxime, $C_{10}H_{16}:NOH$, melting at 91—92°, together with a *compound*, $C_{10}H_{20}N_2O_2$, melting at 162°; but its molecular refractive power favours the view that it is a hydroxy-dihydrocymene (carveol): as such, the hydroxyl group is probably in the position 2. When the last-mentioned compound is reduced with sodium and alcohol, 2-hydroxyhexahydrocymene (tetrahydro-carveol), $C_{10}H_{19}\cdot OH$, is obtained; it boils at 218—220°, has a sp. gr. at $22° = 0.904$, and a specific refractive power $[n]_D = 1.4636$. It combines with carbanil, forming an *urethane* melting at 74—75°, and, when heated at 200° with potassium hydrogen sulphite and, after the addition of alkali, distilled with steam, a hydrocarbon, $C_{10}H_{18}$ (b. p. 175—176°), passes over. When the tetrahydrocarveol is oxidised with chromic acid, a *ketone (tetrahydrocarvone)*, $C_{10}H_{18}O$, boiling at 221°, is obtained; it has a sp. gr. at $20° = 0.904$, and a specific refractive power $[n]_D = 1.45539$, and is optically inactive. On treating the ketone with nascent hydrogen, the tetrahydrocarveol is regenerated. The *oxime*, $C_{10}H_{18}:NOH$, melts at 105°, and, when dissolved in dry chloroform and treated with phosphorus pentachloride, it is converted into an isomeric *compound* melting at 51—52°; the latter, when heated above its melting point, is converted into a third isomeride melting at 104°. When the oxime melting at 105° is reduced with sodium and alcohol, it yields *i*-amido-2-hexahydrocymene, $C_{10}H_{19}NH_2$; this boils at 211—212°, and closely resembles the menthylamines. The *hydro-chloride* melts at 221—222°; the *formyl* derivative, $C_{10}H_{19}\cdot NH\cdot COH$,

obtained by distilling the *formate*, melts at 61—62°; the *acetyl* derivative melts at 124—125°; the *phenylthiocarbamide* derivative, $C_{10}H_{19}$·NH·CS·NHPh, melts at 117°; and the *carbamide* derivative, $C_{10}H_{19}$·NH·CO·NH$_2$, melts at 193—194°.

The compound $C_{10}H_{19}$·OH (see above) must be a secondary alcohol, as it was obtained by the reduction of a ketone, and the hydroxyl group must accordingly occupy positions 2 or 3. In the latter case, it would be *i*-menthol; although the latter compound is unknown, the new alcohol has not a peppermint-like odour, but one recalling that of terpineol, and its boiling point is also considerably higher than that of menthol. The tetrahydrocarveol and its derivatives described by v. Baeyer appear to differ from the author's compounds. Despite these differences, however, the author believes that the compounds described in this paper belong to the carvacrol, and not to the thymol, series. If this be so, the constitution of the above-mentioned trihydroxyhexahydrocymene will be $[(OH)_3 = 1:2:4]$, and that of terpineol 4-hydroxy-Δ^1-tetrahydrocymene.

When pinylamine nitrate (Abstr., 1892, 997) is heated with a solution of sodium nitrite, a secondary *alcohol*, $C_{10}H_{15}$·OH, is obtained; it has a sp. gr. at $22° = 0.978$, a specific refractive power $[n]_D = 1.49787$, has a turpentine-like odour, and boils at 215—218°. On oxidation with chromic acid, it yields a *ketone* which furnishes an *oxime* melting at 98°.

Dihydrocarveol (Abstr., 1893, i, 595) appears to be converted into a trihydroxyhexahydrocymene on oxidation with permanganate; the product is not, however, crystalline, and when warmed with dilute sulphuric acid, yields an oily *oxide*, $C_{10}H_{16}O$, which boils at 196—199°, and has a pleasant, peppermint-like odour; its sp. gr. at 20° is 0.962, and its specific refractive power $[n]_D = 1.484$; it is unsaturated, and appears to react neither with hydroxylamine nor acid chlorides.

<div align="right">A. R. L.</div>

Orientation in the Terpene Series. By A. BAEYER (*Ber.*, **26**, 2558—2565; compare Abstr., 1893, i, 359, 722).—Crystallised terpineol has, according to Wallach (preceding abstract), the formula $CMe{<}^{CH \cdot CH_2}_{CH_2 \cdot CH_2}{>}CPr^\beta \cdot OH$. This position of the hydroxyl group is proved to be correct by the conversion of terpineol into a dihydrocompound which is identical with the tertiary menthol of the formula $CHMe{<}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}{>}CPr^\beta \cdot OH$, previously described by the author. The *methyl ether* of crystallised terpineol, obtained by the action of methylic iodide on the potassium compound, is a mobile liquid which smells like cymene, boils at 212° (corr.), and is immediately oxidised by permanganate. This substance combines with hydriodic acid to form a hydriodide, which, on reduction in ethereal solution with acetic acid and zinc, yields the methyl ether of the tertiary menthol already mentioned. This compound resembles the terpineol methyl ether, but boils at 210°, and is not acted on by permanganate.

Crude terpineol contains an isomeric substance in which the hydroxyl group occupies a different position, since the menthene obtained from the bromide prepared from the crude material is not identical

with that obtained from the crystallised portion. Terpin itself, from which terpineol is prepared, has the formula

$$OH \cdot CMe < ^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2} > CPr^{\beta} \cdot OH,$$
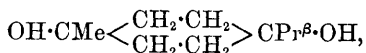
the behaviour of the dibromide towards reducing agents showing that the hydroxyl groups are combined with carbon atoms which are not adjacent. Hence it is probable that the second constituent of crude terpineol has the formula $OH \cdot CMe < ^{CH_2 \cdot CH}_{CH_2 \cdot CH_2} > CPr^{\beta}$. Terpin di-iodide, which might be formed in small quantity by the action of hydriodic acid on terpineol methyl ether, yields, on reduction and hydrolysis of the product, a mixture of menthols which can be separated from menthyl methyl ether by treatment with potassium.

A. H.

Oximes of Cycloïd Ketones. By O. WALLACH (*Annalen*, **277**, 154—161).—When *l*-menthoneoxime (m. p. 59°) is dissolved in chloroform, and phosphorus pentachloride dropped into the solution, an isomeric *oxime* melting at 119—120°, and boiling at 295°, is obtained; its specific rotatory power in alcoholic solution is $[\alpha]_D = -52 \cdot 25°$ at 21°. The *hydrochloride* melts at 91—93°. Menthoneoxime, when warmed with phosphoric anhydride, is converted into a *nitrile*, $C_9H_{17} \cdot CN$, which is an oil having an intense lemon-like odour; its sp. gr. is $0 \cdot 8655$ at 21°, its specific refractive power $[n]_D = 1 \cdot 45609$, and it boils at 220—222°. It is an unsaturated compound, yields an acid forming a sparingly soluble silver salt when boiled with alcoholic potash; and on reduction in alcoholic solution with sodium, an *amido*-compound, boiling at 210—215°, is obtained. The isomeric oxime (m. p. 105°; this vol., i, 44) can also be converted into a nitrile.

Thujonoxime melts at 54—55°, and when treated as above with phosphorus pentachloride, is converted into an *isomeride* melting at 90°; it likewise yields a *nitrile* when warmed with phosphoric anhydride.

Pulegonoxime melts at 118—119°, and the ketone regenerated from it by treatment with dilute sulphuric acid boils at 220—225°, has a sp. gr. $0 \cdot 933$, and a specific refractive power $[n]_D = 1 \cdot 47974$ at 21°. When the oxime is reduced in alcoholic solution with sodium, a *base* is obtained which is perhaps identical with *l*-menthylamine.

A. R. L.

Formation of Trimethylsuccinic acid from Camphoric acid. By W. KOENIGS (*Ber.*, **26**, 2337—2340).—Camphoric acid was oxidised by dissolving it in very dilute aqueous soda, and allowing the solution to drop into a boiling solution of chromic and sulphuric acids. The products were carbonic anhydride and camphoronic acid, together with small quantities of an acid which melts with decomposition at 220—222°, of acetic acid, and of the trimethylsuccinic acid synthesised by Bischoff (Abstr., 1891, 828). The anhydride of this last acid is volatile with steam.

When camphoroxime is oxidised by heating with rather dilute nitric acid, the products are camphoric acid, a nitrogenous substance melting at 215—218°, and Thiel's isocamphoronic acid (Abstr., 1893, i, 423).

C. F. B.

Sulphocamphylic acid. By W. KOENIGS and J. HOERLIN (*Ber.*, **26**, 2044—2050; compare Abstr., 1893, i, 363).—Sulphocamphylic acid is readily oxidised by hot nitric acid (sp. gr. 1·25) with production of oxalic, dimethylmalonic, and sulphoisopropylsuccinic acids. The two former acids are extracted by ether, and the latter is isolated by precipitating its lead salt with hydrogen sulphide. *Sulphoisopropylsuccinic acid*, $C_7H_{12}SO_7,H_2O$, forms large, lustrous, tabular, colourless crystals melting at 167° with decomposition ; it is readily soluble in water or alcohol, but only sparingly in ethylic acetate, chloroform, or benzene. It is a tribasic acid yielding easily soluble salts; the *barium* salt forms an amorphous, vitreous mass containing water, which is lost at 190—200°. The acid yields terebic acid, sulphurous anhydride, and water at 160—170° ; a small quantity of an easily soluble *acid*, which melts at 137—138° and contains no sulphur, also distils.

From the formation of dimethylmalonic acid during the oxidation of sulphocamphylic acid, Koenigs infers that camphor must contain the group $CMe_2{<}^C_C$.   W. J. P.

Xanthorrhœa Resins. By M. BAMBERGER (*Monatsh.*, **14**, 333—343).—Yellow Xanthorrhœa resin (*X. hastilis*, Sm.) was extracted with boiling 95 per cent. alcohol, the residue repeatedly boiled with water, and finally dissolved in dilute potash and acidified with dilute sulphuric acid. The crystalline material obtained from these various extracts by means of ether was then treated with chloroform, in which it partially dissolved. The portion insoluble in chloroform, on purification, proved to be paracoumaric acid, $C_9H_8O_3 + H_2O$, about 10 per cent. of the weight of the resin being obtained. The portion of the extract which was soluble in chloroform contained parahydroxybenzaldehyde, benzoic acid, and cinnamic acid. A small quantity of a substance, which was probably vanillin, was also isolated, as well as a small quantity of a white neutral substance, the nature of which was not further examined. Red Xanthorrhœa resin (*X. australis*), when treated in the same manner, yielded about 2 per cent. of paracoumaric acid, together with parahydroxybenzaldehyde and a substance resembling vanillin. Cinnamic and benzoic acids were not detected in this resin.   A. H.

Iridin, the Glucoside of Violet Roots. By G. DE LAIRE and F. TIEMANN (*Ber.*, **26**, 2010—2044).—The dried roots of the violet (*Iris florentina*), on extraction with alcohol, yield a glucoside *iridin*, $C_{24}H_{26}O_{13}$; it forms slender, white needles, melts at 208°, and turns yellow in the air. Iridin undergoes hydrolysis when heated with dilute sulphuric acid at 80—100°, yielding *d*-glucose and *irigenin*, $C_{18}H_{16}O_8$. This substance crystallises in rhombohedra, melting at 186°. *Dibenzoylirigenin*, $C_{18}H_{14}O_9Bz_2$, is a white, crystalline powder melting at 123—126°, whilst *diacetylirigenin* is a white, crystalline powder melting at 122° ; the latter forms a compound with chloroform, which is obtained in beautiful white leaflets melting at 82°. *Acetylirigenin*, $C_{18}H_{15}O_8Ac$, is prepared by warming

the diacetyl derivative with soda, and crystallises in white needles melting at 169°.

On heating irigenin with concentrated potash, in absence of air, formic acid, iridic acid, and iretol are obtained in molecular proportion.

Iridic acid, $OMe \cdot C \underset{C(OH)-CH}{\overset{C(OMe):CH}{<}} > C \cdot CH_2 \cdot COOH$, forms colourless prisms melting at 118°, and when heated above its melting point evolves carbonic anhydride and yields iridol. It is a strong monobasic acid, giving a well-crystallised *barium* salt, $Ba(C_{10}H_{11}O_5)_2, 5H_2O$; the *calcium* salt and those of the alkali metals are very hygroscopic. The *methylic* salt is a viscid oil boiling above 360°, whilst the *ethylic* salt is a yellow oil which decomposes on distillation under ordinary pressure. *Benzoyliridic acid,* $C_{10}H_{11}O_5Bz$, melts at 131°, and the corresponding *acetyl* derivative at 125°.

Methyliridic acid, $C_6H_2(OMe)_3 \cdot CH_2 \cdot COOH$, forms white leaflets melting at 120°; its *silver* salt separates from alcohol in beautiful white needles.

Iridol, $OMe \cdot C \underset{C(OMe) \cdot CH}{\overset{C(OH):CH}{<}} > CMe$, distils on heating iridic acid at 239°; it forms large, white needles melting at 57°. The *benzoyl* derivative forms white leaflets melting at 68°.

Methyliridol, $C_6H_2Me(OMe)_3$, is a colourless oil boiling at 236—237°, and on oxidation with dilute permanganate gives $3:4:5$-trimethylgallic acid; it is, therefore, the trimethyl derivative of homopyrogallol. Further, on treating iridol with chloroform and caustic alkali, two isomeric aldehydes are obtained; iridol, therefore, being a dimethylhomopyrogallol, can only have the constitution assigned to it above. Iridol is isomeric with a dimethylhomopyrogallol isolated from woodtar by Hofmann (Abstr., 1880, 248), which has the constitution $Me : OH = 1 : 4$, and may be oxidised to eupitonic acid; as would be expected from the constitution assigned to it, iridol does not yield this acid or an isomeric one under similar conditions. Both iridol and Hofmann's phenol give the same trimethylhomopyrogallol on methylation, and the same trimethylgallic acid on eliminating the methyl group from the nucleus.

Dibromomethyliridic acid, $C_6Br_2(OMe)_3 \cdot CH_2 \cdot COOH$, is obtained by direct bromination, and forms hard crystals melting at 152°; it is very soluble in alcohol or ether. On oxidation with nitric acid, it yields *dibromotrimethylgallic acid*, which crystallises in long, brilliant needles melting at 143°. On oxidising methyliridic acid with permanganate, trimethylgallic acid is ultimately obtained, but by careful operation an *α-ketonic acid* of the composition $C_6H_2(OMe)_2 \cdot CO \cdot COOH$ may be isolated as an intermediate product. The constitutional formulæ assigned above to iridic acid and its methyl derivative are thus determined.

Iretol, $C_6H_2(OH)_3 \cdot OMe$ [$= 2 : 4 : 6 : 1$], is obtained by adding excess of sulphuric acid to the product obtained by heating irigenin with caustic alkali, neutralising with potassium carbonate, and repeatedly extracting with ether. On evaporating the ethereal solution, iretol remains, and is ultimately obtained in white needles melting at

186°; it is soluble in water, alcohol, ether, and ethylic acetate, and has the normal molecular weight in acetic acid solution. Its *tribenzoyl* derivative, $C_6H_2(OBz)_3 \cdot OMe$, forms a resin. On reduction with sodium amalgam, iretol yields phloroglucinol; it therefore has the constitution stated above. *Tribenzoylphloroglucinol* crystallises in white needles melting at 172°. Iretol gives the phenolic test with ferric chloride, and combines with diazobenzene salts with formation of an insoluble red *azo*-compound; it also condenses with benzaldehyde, and with strong oxidising agents gives oxalic acid. On treatment with bromine, in absence of water, it gives hexabromacetone, and with a solution of bromine in caustic alkali, it yields bromoform. It reacts violently with phenylhydrazine or hydroxylamine; no crystalline products of these reactions could be isolated.

Sodiodinitrosoiretol, $OMe \cdot C \underset{C(OH)-C(NOH)}{\overset{CO-\!\!-\!\!-C(NONa)}{<}} > CO, H_2O$, separates as small, red crystals on treating an aqueous solution of iretol with sodium nitrite and acetic acid; it dissolves in hot water, alkalis, or acids, giving a deep red solution. On heating at 106°, it loses $2H_2O$, leaving an anhydride of the constitution $\begin{array}{l} CO \cdot C(OMe) : C-\!\!-O \\ C(NONa) \cdot CO \cdot C \!\!=\!\! N \end{array}$, and explodes at a higher temperature.

$1:2:3:5$-*Tetrhydroxybenzene* is prepared by heating iretol at 130—150° in sealed tubes with dilute hydrochloric acid; it is ultimately obtained as a syrup which slowly solidifies to an amorphous, glassy mass.

Sodiotetramethyliretol, $OMe \cdot C \underset{CO-\!\!-\!\!-CMe_2}{\overset{C(ONa) \cdot CMe_2}{<}} > CO, 3H_2O$, is obtained by heating iretol with sodium methoxide, methylic iodide, and methylic alcohol; it is precipitated by ether from its alcoholic solution in long, white needles which lose $3H_2O$ in a vacuum or at 100°. On treatment with dilute sulphuric acid, it yields *tetramethyliretol*, which forms lustrous, transparent, colourless needles containing $1H_2O$, and melting at 97°. The anhydrous substance melts at 104°; its *benzoyl* derivative forms white leaflets melting at 84°. Tetramethyliretol yields formic, isobutyric, and dimethylmalonic acids when fused with potash; its constitution is thus determined. On reducing its sodio-derivative with sodium amalgam in aqueous solution, *dihydrotetramethyliretol*, $OMe \cdot CH \underset{CO-\!\!-\!\!-CMe_2}{\overset{CH(OH) \cdot CMe_2}{<}} > CO, H_2O$, is obtained as its *sodio*-derivative, which forms a crystalline meal. On acidifying and extracting with ether, the phenol is set free and crystallises from water in transparent rhombs melting at 107°; it loses $1H_2O$ in a vacuum, yielding the anhydrous substance, which melts at 139° and sublimes at ordinary temperatures. It is very soluble in water, alcohol, ether, or chloroform, and is readily acted on by bromine water or permanganate.

Dehydroditetramethyliretol,

$$CO \underset{CMe_2 \cdot CO}{\overset{CMe_2 \cdot CO}{<}} > C(OMe) \cdot C(OMe) C \underset{CO \cdot CMe_2}{\overset{CO \cdot CMe_2}{<}} > CO,$$
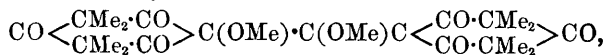
separates on warming sodiotetramethyliretol with ferric chloride

solution; it forms slender, white needles melting at 133°, is readily soluble in alcohol, ether, benzene, or chloroform, but insoluble in water, and is not at once attacked by bromine or permanganate in acetic acid solution. It has the normal molecular weight in boiling alcohol.

Pentamethyliretol, $OMe \cdot CMe < \begin{matrix} CO \cdot CMe_2 \\ CO \cdot CMe_2 \end{matrix} > CO$, is formed on heating sodiotetramethyliretol with methylic iodide and methylic alcohol at 100°; it crystallises in long needles, melts at 62°, boils at 240°, and is volatile in a current of steam.

Methyliretol, $C_6H_2(OMe)_2(OH)_2$ [$(OMe)_2 : (OH)_2 = 1:4:2:6$ or $1:2:4:6$], is prepared by saturating a solution of iretol in methylic alcohol with hydrogen chloride; it is ultimately obtained in white leaflets melting at 87°.

Tetrethyliretol is precipitated by light petroleum from its chloroform solution in white prisms melting at 168—169°.

A *tripotassio*-derivative of the composition $C_{24}H_{25}K_3O_{14}$ is obtained by acting on an alcoholic solution of iridin with excess of potassium ethoxide; if less of the latter reagent is used, a *dipotassio*-derivative, $C_{24}H_{26}K_2O_{14}$, is formed. The corresponding *disodio-* and *trisodio-* compounds were also prepared; these substances form scarcely crystalline, very hygroscopic, white powders. The first product of hydrolysis of iridin therefore has the formula $C_{18}H_{14}O_5(OH)_3 \cdot OC_6H_{11}O_5$, and consequently the hydrolysis of irigenin gives primarily an *α-diketone* containing four hydroxyl groups; this, on treatment with potassium cyanide in alkaline solution, gives an aldehyde and an acid, just as does benzene (Jourdan, *Ber.*, **24**, 658). On warming irigenin with dilute potash and acidifying, a precipitate is obtained which is dissolved in alcohol; on evaporating, unaltered irigenin separates, and the mother liquor, containing the products of hydrolysis, is treated with soda and potassium cyanide. After acidification, the solution is extracted with ether and a syrupy *aldehyde* is isolated from the ethereal solution by means of its compound with sodium hydrogen sulphite. The same aldehyde is obtained by treating iretol with potash, alcohol, and chloroform at the ordinary temperature; when heated with caustic alkali at 100°, it gives formic acid and iretol. These same products, together with iridinic acid, are obtained on heating irigenin with alkali. The first product of the hydrolysis of irigenin should consequently have the constitution

$$OH \cdot C_6H_2(OMe)_2 \cdot CH_2 \cdot CO \cdot CO \cdot C_6H_2(OH)_3 \cdot OMe.$$
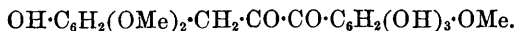
Irigenin can then only be considered as having the constitution

$$OMe \cdot C \begin{matrix} C(OMe):CH \\ C(OH) \cdot CH \end{matrix} > C \cdot CH_2 \cdot \begin{matrix} O------C \cdot C(OMe) \\ C \cdot CO \cdot C \\ O------C === CH \end{matrix} > C \cdot OH,$$
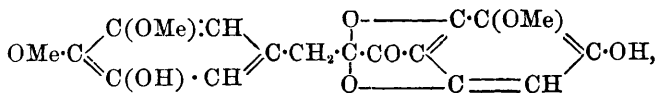
and iridin must be represented as

$$\text{OMe·C}\diagdown^{\text{C(OMe):CH}}_{\text{C(OH)·CH}}\diagup\text{C·CH}_2\text{·}\overset{|}{\underset{|}{\text{C}}}\text{·CO·C}\diagdown^{\text{O———C·C(OMe)}}_{\text{O———C═══CH}}\diagup\text{C·OC}_6\text{H}_{11}\text{O}_5.$$
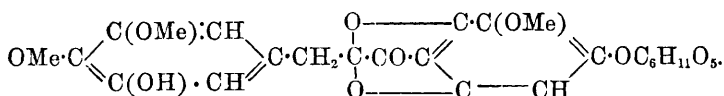
The qualitative solubilities of the substances are given in detail in the original. W. J. P.

Paracotoïn. By G. CIAMICIAN and P. SILBER (*Ber.*, **26**, 2340—2348).—Paracotoïn, from paracoto bark, was found by analysis and molecular weight determination to have the composition $C_{12}H_8O_4$ (probably $CH_2{:}O_2{:}C_6H_3{\cdot}C_5H_3O$), and not $C_{19}H_{12}O_6$, as is stated by Jobst and Hesse (Abstr., 1880, 326); it crystallises in yellow plates melting at 151—152°. With concentrated nitric acid, it yields *dinitroparacoton*, $C_{12}H_6(NO_2)_2O_4$, forming yellow needles melting at 195°. With bromine in chloroform solution, it yields an unstable additive compound; this is converted by treatment with sulphurous anhydride into *bromoparacoton*, $C_{12}H_7BrO_4$, a substance which forms thick crystals with adamantine lustre, and melts at 200—201°. With phenylhydrazine, it does not react in acetic acid solution, but, if no third substance is present, a compound, $C_{24}H_{22}N_4O_3$, is formed, which crystallises in nodular aggregates of needles, and melts at 200—201°. With aniline (2 mols.), it forms an additive compound, $C_{24}H_{22}N_2O_4$, crystallising in nodular aggregates, and melting at 162°. Fusion with solid potash converts paracotoïn into piperonylic acid, acetopiperone, protocatechuic, formic, and another fatty (? butyric) acid. When treated with methyl alcoholic potash and methylic iodide, paracotoïn yields *dimethylparacotoin*, $C_{12}H_6Me_2O_4$; this forms lustrous, yellow crystals, melts at 141°, and, with bromine, yields an unstable additive compound, from which the original substance is readily regenerated. Dimethylparacotoin contains no methoxyl, for it does not yield methylic iodide when heated with hydriodic acid, and is converted by aqueous potash into the homoacetopiperone (melting at 38°) of Angeli (Abstr., 1892, 1199); the authors think this last substance is more probably propiopiperone, $CH_2{:}O_2{:}C_6H_3{\cdot}CO{\cdot}CH_2Me$. C. F. B.

Santonin. By J. KLEIN (*Ber.*, **26**, 2506—2508).—By the distillation of santonin, a compound is obtained which is soluble in alkali, and crystallises from dilute alcohol in plates; it melts at 97—98°, and has the formula $(C_{12}H_{13}O)_2$. The yield is small. Oxysantogenenic acid, in a similar manner, yields a compound $C_{12}H_{14}O$, which crystallises in needles, melts at 111—112°, and appears to be identical with Cannizzaro's hydrodimethylnaphthol. On heating oxysantogenenic acid at about 360°, a white powder is formed, which dissolves in chloroform, and is precipitated by alcohol; it has the same composition as oxysantogenenic anhydride, $(C_{15}H_{21}O_2)_2O$. The production of this compound is incompatible with Cannizzaro's explanation of the decomposition of santogenenic acid, since this acid has the formula $C_{15}H_{22}O_3$, and is identical with oxysantogenenic acid. α-Santogendilactone, $(C_{15}H_{18}O_2)_2O$, on distillation, yields a hydrocarbon $(C_{14}H_{18})_2$ which crystallises from ether-alcohol in needles, and melts at 93°. The ketonic group in santonin must, therefore, be in the side chain

(compare Abstr., 1893, i, 664); the hydroxyl of the two naphthols (see above) does not correspond with that of santoninic acid or santonous acid, but is linked to that carbon atom to which, in the original substance, the side chain is attached. This is a further reason for rejecting Cannizzaro's theory.   J. B. T.

Constitution of Santonous acid. By S. CANNIZZARO (*Ber.*, **26**, 2311—2312; compare Andreocci, Abstr., 1893, i, 526).—By the action of potash at 220° on potassium desmotroposantonate a lactone is formed, which is isomeric with desmotroposantonin, and is, therefore, termed *isodesmotroposantonin;* it melts at 187—188°, and its rotatory power is +127·55°. These compounds have identical structural formulæ, and yield isomeric acetyl derivatives, and also two desmotroposantonous acids and two isodesmotroposantonous acids which are unstable. *Isodesmotroposantonous acid* is the optical isomeride of santonous acid; each melts at 177—179°; the rotatory power of the former is −74·30°, that of the latter +74 36°; a mixture of the two in equal molecular proportions is inactive, melts at 153°, and is identical with isosantonous acid. The *ethylic salts* of the active acids melt at 116—117°, their rotatory power is −70·37° and +70·57° respectively, and they crystallise in similar forms. On admixture, the two salts combine to form a racemic compound which melts at 125°, and is identical with ethylic isosantonate. The methylic salts closely resemble the ethylic salts, and exhibit similar relationships.   J. B. T.

2-Chloroquinoline. By A. CLAUS and R. KAYSER (*J. pr. Chem.*, [2], **48**, 270—285).—2-Chloroquinoline dichromate is more soluble than 4-chloroquinoline dichromate, and remains in solution after the latter has been crystallised (see next abstract). The base is liberated by an alkali, and fractionally distilled in steam ; it boils at 256°, and melts at 45° ; it has not heretofore been crystallised, because the dichromate had not been purified, but had only been prepared in a condition in which its melting point is 109°, that of the pure salt being 121°. The *oxalate*, which melts at 145°, is a good source of the pure base. Evidence of the orientation of this chloroquinoline accrues from its preparation by Claus and Massau from 2-nitroquinoline (Abstr., 1893, i, 670). The *platinochloride* forms lustrous, yellow needles, which become darker, and melt at 255°. The *argentonitrate* melts at 120°, and dissolves in hot alcohol and hot water. The *methiodide* crystallises in long, lustrous, yellow needles, and decomposes at 172°. The *methochloride* forms small needles, which easily become coloured reddish-yellow, and melts at 122° ; its *platinochloride* melts with decomposition at 246°.

1 : 2-*Nitrochloroquinoline* is prepared by nitrating the chloroquinoline with a mixture of nitric and sulphuric acids; it crystallises in large, vitreous, yellow needles and prisms, melts at 138°, and sublimes in colourless needles ; it dissolves easily in organic solvents and in concentrated acids. The basic properties of the 2-chloroquinoline are enfeebled by the introduction of the nitro group, so that no methiodide is obtainable. The *platinochloride* is described.

1 : 2-*Amidochloroquinoline* crystallises in colourless, or slightly yellow, vitreous needles, melts at 114°, and dissolves freely in organic solvents, but only sparingly in water. It shows the feeble, basic properties characteristic of all 1-amidoquinolines; thus, it dissolves in moderately strong hydrochloric acid, with a reddish-yellow colour, which is discharged on shaking the liquid with ether, owing to the extraction of the base by this solvent; mere dilution of the hydrochloric acid solution with water will precipitate the base. The *hydrochloride*, $C_9NH_5Cl\cdot NH_2,HCl$, crystallises in needles, and melts at 221°. The *platinochloride* melts, with decomposition, at 246°. The *stannochloride* forms orange-red crystals, and melts at 173°.

1 : 2-*Dichloroquinoline*, obtained through the diazo-reaction, crystallises in colourless, lustrous needles, and melts at 85·5°. Its *platinochloride* is described.

A second nitro-derivative, apparently 4 : 2-*nitrochloroquinoline*, is obtained by neutralising the nitrating liquor from which the 1 : 2-derivative has separated; it melts at 115°.

2 : 1-*Chloroquinolinesulphonic acid*, obtained by sulphonating the chloroquinoline at 150° with 30 per cent. anhydrosulphuric acid, crystallises in soft, colourless needles, and decomposes about 350°; it is insoluble in most organic solvents, but dissolves slightly in alcohol and considerably in hot water. The *ammonium* salt, the *potassium* salt, the *silver* salt, the *chloride* (m. p. 137°), and the *amide* (m. p. 122°) were prepared. By reduction with tin and hydrochloric acid, a tetrahydroquinoline derivative, melting at 243—244°, was obtained, thus confirming the orientation. A. G. B.

4-Chloroquinoline. By A. CLAUS and K. JUNGHANNS (*J. pr. Chem.*, [2], **48**, 253—266).—La Conte (Abstr., 1886, 159) prepared 2- and 4-chloroquinoline, but did not succeed in separating them completely. Freydl (Abstr., 1888, 296) described derivatives of 4-chloroquinoline as those of 2-chloroquinoline.

The two chloroquinolines are separated by conversion into dichromates, of which the 4-chloroquinoline dichromate crystallises first (compare preceding abstract). It melts with decomposition at 178°.

4-Chloroquinoline forms a stellate, crystalline mass, or separate prismatic crystals, melts at 31°, boils at 268°, and dissolves slightly in hot water and freely in organic solvents. The *platinochloride* forms lustrous, orange-yellow needles; the *argentonitrate* forms flat, colourless needles, and melts at 154°; the *methiodide* melts with decomposition at 250°; the *methochloride* melts with decomposition about 213°, and its *platinochloride* melts with decomposition at 238°.

1 : 4-*Nitrochloroquinoline* crystallises in colourless, vitreous, transparent prisms, melts at 184°, and dissolves easily in alcohol, ether, chloroform, and concentrated acids, but not in water. The *platinochloride* melts with decomposition at 221°.

1 : 4-*Amidochloroquinoline*, obtained from the nitro-derivative in the usual manner, crystallises in colourless, vitreous needles, melts at 69°, and sublimes; it dissolves in organic solvents, but only very slightly in water. The *hydrochloride*, $C_9NH_5Cl\cdot NH_2,HCl$, forms

yellowish crystals, and melts at 115—116°; its solution in hydro-chloric acid is intensely red. The *platinochloride* melts with decomposition at 160°. On treatment by Sandmeyer's method, the amido-derivative is converted into 1 : 4-dichloroquinoline (Abstr., 1893, i, 688).

During the nitration of 4-chloroquinoline, a second *nitro*-derivative is formed; it is isolated by neutralising the acid liquor, and can be crystallised in nearly colourless needles. It melts at 128°, and is more soluble in hot water than 1 : 4-nitrochloroquinoline; a *platinochloride* was prepared.

4 : 1-*Chloroquinolinesulphonic acid* is obtained when 4-chloroquinoline is heated with 30 per cent. anhydrosulphuric acid at 150° for 10 hours. It crystallises in colourless, rhombic tables, and decomposes, without melting, at about 350°; it is insoluble in absolute alcohol and in ether, and only moderately soluble in hot water. The *potassium* salt, with $1H_2O$, the *sodium* salt, the *calcium* salt, the *barium* salt, the *ammonium* salt, the *silver* salt, the *chloride*, $C_9NH_5Cl\cdot SO_2Cl$ (m. p. 146°); the *amide*, $C_9NH_5Cl\cdot SO_2NH_2$ (m. p. 178°); and the *ethylic* salt, $C_9NH_5Cl\cdot SO_2OEt$ (m. p. 85°) are described.   A. G. B.

1 : 4-Nitrobromoquinoline. A Correction. By A. CLAUS and G. N. VIS (*J. pr. Chem.*, [2], **48**, 267—269).—In an earlier communication (Abstr., 1890, 173), the authors described 3 : 4-nitrobromoquinoline and 3 : 4-amidobromoquinoline. This orientation was deduced from the conversion of these compounds into a dibromoquinoline, which was found to melt at 124°, and was, therefore, supposed to be 3 : 4-dibromoquinoline, inasmuch as 1 : 4-dibromoquinoline was known to melt at 127—128°. They now find that they were in error when ascribing the melting point 124° to this dibromoquinoline; it is now found to be 127—128°, and, consequently, the proper orientation of the nitro- and amido-bromoquinoline should be 1 : 4, not 3 : 4.   A. G. B.

Oxazine Derivatives from Orthamidophenol and Hydroxyquinones. By F. KEHRMANN and J. MESSINGER (*Ber.*, **26**, 2375—2376).—Derivatives of phenoxazine may be prepared by the condensation of orthamidophenol with many hydroxyquinones. Monochloroparadihydroxyquinone, for example, yields

$$OH\cdot C_6ClO{<}^N_O{>}C_6H_4.$$
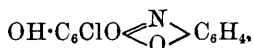
The product, which the authors term *chlorhydroxyphenoxazone*, crystallises from alcohol or acetic acid in yellowish-brown needles, and dissolves in alkalis and alkaline carbonates. It melts at 235° with decomposition. Acetic anhydride converts it into an *acetyl* derivative which crystallises in brownish-red needles with a green lustre, and melts at about 200° with decomposition.

The authors propose to extend the reaction described in this preliminary notice to a number of hydroxyquinones and monalkylorthamidophenols.   A. H.

Action of Picrylic Chloride on Monalkylorthodiamines. By F. Kehrmann and J. Messinger (*Ber.*, **26**, 2372—2375).—Picrylic chloride acts on the monalkyl derivatives of the orthodiamines in the same way as on orthamidophenol (Turpin, Trans., 1891, 714),

$$C_6H_2(NO_2)_3Cl + C_6H_4(NH_2)NH\cdot R = C_6H_2(NO_2)_3\cdot NH\cdot C_6H_4\cdot NHR.$$

The substituted picrylorthophenylenediamines thus produced can readily be isolated, and are converted by boiling with alcohol into the corresponding dinitrodihydrophenazines, nitrous acid being eliminated.

n-Methyldinitrodihydrophenazine, $C_6H_2(NO_2)_2<^{N\cdot Me}_{NH-}>C_6H_4$, forms dark violet, flaky crystals with a cupreous lustre. It melts with decomposition at 240°, and is readily soluble in hot ethylic benzoate, but only slightly in other solvents. The cold solutions are olive-green, but become an intense reddish-violet when heated. It dissolves without change in sulphuric acid, and forms a deep blue solution in cold alcoholic potash. The solution in acetic acid decomposes on boiling, nitric oxide being evolved. *n-Ethyldi-nitrodihydrophenazine* forms small needles resembling sublimed indigo, and melts at 246° with decomposition. In solubility, it resembles the methylic derivative. *n-Benzyldinitrodihydrophenazine* separates from boiling benzene in tablets which have a violet metallic lustre, and melts at 240° with decomposition. *n-Phenyldinitrodihydrophenazine* prepared from orthamidodiphenylamine melts at 246°.

Dinitrodihydrophenazine, $C_6H_2(NO_2)_2<^{NH}_{NH}>C_6H_4$, can be obtained with some difficulty from the product of reaction of orthophenylene-diamine and picrylic chloride.　　　　　　　　　　A. H.

Hippuroflavin. By L. Rügheimer and A. Küsel (*Ber.*, **26**, 2319—2327).—Hippuroflavin, $^{CO-C---NBz}_{NBz\cdot C---CO}$, has been previously prepared by the action of phosphorus pentachloride on ethylic hippurate (*Ber.*, **21**, 3321); an intermediate compound, $CPhCl:N\cdot CHCl\cdot COOEt$, is first formed, and hydrogen chloride and ethylic chloride are then eliminated. In support of this view, the authors have obtained *ethylic hydroxyhippurate*, $NHBz\cdot CH(OH)\cdot COOEt$, by treating the product formed by heating ethylic hippurate and phosphorus pentachloride at 140°, with ice; it crystallises in small, colourless needles melting at 114—115°. Hippuroflavin resembles quinone in some of its reactions, and yields unstable additive products with phenols, and stable compounds with aniline bases. With ordinary phenol, the compound $C_{18}H_{10}N_2O_4,2C_6H_5OH$ is formed, and crystallises in colourless needles; it is resolved into its constituents on heating or by boiling with dilute alcohol. *Dianilidohippuroflavin,* $NBz<^{CO\cdot C(NHPh)}_{C(NHPh)\cdot CO}>NBz$, is formed by boiling hippuroflavin with aniline in excess; it is sparingly soluble, crystallises from benzene or glacial acetic acid in pale yellow needles, and melts at 234·5—235·5°. By the action of

alcoholic potash, it is decomposed with formation of ammonia; with aqueous alkalis, it undergoes hydrolysis, two acids being obtained. The one is monobasic, has the formula $\begin{matrix} CO \cdot C(NHPh) \cdot NHBz \\ NBz \cdot C(NHPh) \cdot COOH \end{matrix}$ and crystallises from alcohol in small needles which melt at 226—227° with decomposition. The second acid, which is bibasic, appears to be *dibenzamidodianilidosuccinic acid,*

$$COOH \cdot C(NHPh)(NHBz) \cdot C(NHPh)(NHBz) \cdot COOH,$$
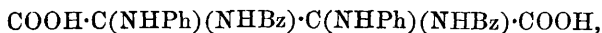
and crystallises in broad, stellate needles melting at 221—222°. *Anilidohippuroflavin,* $\begin{matrix} CO-CH----NBz \\ NBz \cdot C(NHPh) \cdot CO \end{matrix}$, is obtained together with the dianilide; it crystallises in small, yellow needles, and melts at 189—192°. Toluidine, xylidine, and methylaniline also react with hippuroflavin, giving compounds corresponding with the monoanilide; dimethylaniline does not combine with hippuroflavin. The formation of the above anilido-compounds does not take place directly, but is preceded by that of *dihydroxydianilidohippuroflavin,*

$$NBz < \begin{matrix} C(OH) \cdot C(NHPh) \\ C(NHPh) \cdot C(OH) \end{matrix} > NBz;$$
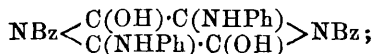
this is a colourless substance, and melts at 258—260°. The corresponding orthotoluidine derivative crystallises from glacial acetic acid, and melts at 235—238°. Both compounds are almost insoluble in ordinary media, they are feebly basic (phenolic), dissolve in alcoholic potash, and are reprecipitated on the addition of water. On heating with alcoholic potash or nitrobenzene, hydrogen is eliminated, and the yellow anilido-derivatives are formed. It is at present uncertain whether the C(OH)C(NHPh) groups in dihydroxydianilidohippuroflavin are doubly linked in the ortho- or para-position. J. B. T.

Action of Thionic, Phthalic, and Succinic Chlorides on Phenylhydrazine. By M. FREUND and S. WISCHEWIANSKY (*Ber.*, **26,** 2494—2496).—*Thionyl-ψ-diphenylthiocarbazone,* $\begin{matrix} SO-S \\ NPh \cdot N \end{matrix} > C \cdot N_2Ph,$ is prepared by the action of thionic chloride on diphenylthiocarbazone in benzene solution at ordinary temperatures, and is deposited from benzene-alcohol in yellow crystals which melt at 144—145°. It is stable towards aqueous alkalis, but, on boiling with alcohol or alcoholic potash, is resolved into its components. The letter ψ is employed by the authors to indicate that the phenylhydrazine derivative reacts in its pseudo-form. By the treatment of the carbazone with alcoholic ammonic sulphide, it is converted into *thionyl-ψ-diphenylcarbizine,* $C_{13}H_{12}N_4S_2O$, which is crystalline, melts at 162°, and is readily oxidisable. *Phthalyl-ψ-diphenylcarbazone,*

$$\begin{matrix} CO \cdot O \\ C_6H_4 \end{matrix} > C < \begin{matrix} S---C \cdot N_2Ph \\ NPh \cdot N \end{matrix}$$
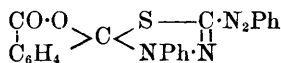
is prepared from phthalic chloride and diphenylthiocarbazone, and

crystallises from alcohol or glacial acetic acid in yellow plates melting at 182°; the compound is resolved into its components by treatment with alcoholic potash. Succinyldiacetylphenylhydrazine is prepared from succinic chloride and acetylphenylhydrazine, and has been previously obtained by Michaelis. *Succinyldiformylphenylhydrazine*, $C_2H_4(CO\cdot NPh\cdot NH\cdot CHO)_2$, is formed from succinic chloride and formylphenylhydrazine; it is crystalline, and melts at 246—247°. No definite compounds could be obtained by the action of succinic chloride on diphenylsulphocarbazone or of thionic chloride on acid derivatives of phenylhydrazine. J. B. T.

Triazole Derivatives from Amidoguanidine. By J. Thiele and K. Heidenreich (*Ber.*, **26**, 2598—2602).—*Amidomethyltriazole*,

$NH_2\cdot C{<}^{NH\cdot N}_{N-CMe}$, is obtained by dissolving acetamidoguanidine nitrate (Abstr., 1892, 1297) in aqueous sodium carbonate, and evaporating the solution to dryness; it crystallises from boiling glacial acetic acid in stellate groups of white needles, and melts at 148°; the *silver* salt is insoluble in water; the *nitrate* melts at 171°; and the *picrate* melts at 225° with decomposition.

Azomethyltriazole, $^{N-NH}_{CMe\cdot N}{>}C\cdot N{:}N\cdot C{<}^{NH\cdot N}_{N-CMe}$, is formed when the amido-derivative is oxidised with permanganate in presence of a large excess of alkali; it dissolves in alkalis, but is insoluble in all indifferent solvents, forms a yellow powder, and decomposes at a very high temperature without melting. The *silver* salt is a voluminous precipitate. When the azo-derivative is reduced with stannous chloride, *hydrazomethyltriazole* is obtained; the *hydrochloride* crystallises in six-sided prisms, is sparingly soluble in concentrated hydrochloric acid, insoluble in alcohol and ether, and melts at 250° with decomposition. A. R. L.

New Triazole and Triazine Derivatives. By O. Widmann

(*Ber.*, **26**, 2612—2617).—*Hydroxyphenyltriazole*, $NPh{<}^{CH:N}_{N-COH}$, is obtained by boiling phenylsemicarbazide with concentrated formic acid ($2\frac{1}{2}$ parts) in a reflux apparatus for $7\frac{1}{2}$ hours; it is almost insoluble in nearly all ordinary solvents, and melts at a very high temperature. The *hydrochloride*, $C_8H_7N_3O,HCl + H_2O$, crystallises in fan-shaped groups of needles. When the *silver* salt, $C_8H_6N_3\cdot OAg + H_2O$, is strongly heated, phenyltriazole sublimes and a residue of metallic silver remains; the same phenyltriazole is also obtained by heating the hydroxy-derivative with phosphoric sulphide; it agrees in properties with Andreocci's phenylpyrrodiazole (Abstr., 1892, 636). The *platinochloride*, $(C_8H_7N_3)_2,H_2PtCl_6$, if heated at 180°, becomes a paler yellow with the loss of hydrogen chloride (2 mols.), and the formation of the salt $(C_8H_7N_3)_2,PtCl_4$.

Diphenyltetrahydrotriazine, $NPh{<}^{CO\cdot CH_2}_{N=CH}{>}NPh$, is obtained by boiling α-phenylamidacetylphenylhydrazide,

$$NPh(CO \cdot CH_2 \cdot NHPh)NH_2,$$
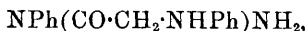
with anhydrous formic acid; it melts at 173—174°. A. R. L.

Constitution of the Triazole and Tetrazole Derivatives prepared by Andreocci and by Bladin. By O. WIDMANN (*Ber.*, **26,** 2617—2621).—The hydroxyphenyltriazole described in the last abstract is isomeric with Andreocci's compound (*Reg. Univers. d. Studi Roma*, 1890—1891, 469), and must have the constitution,

$$NPh{<}^{CO \cdot NH}_{N\,:\,CH},$$
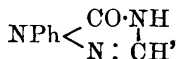
assigned to it by this chemist, and not that proposed by Bladin. The formulæ of all Bladin's triazole and tetrazole derivatives require alteration. It also follows that dicyanophenylhydrazine has the constitution $NHPh \cdot N{:}C(CN) \cdot NH_2$. (Compare this vol., i, 23.)

A. R. L.

Narceïne. By M. FREUND and G. B. FRANKFORTER (*Annalen,* **277,** 20—58).—The authors find that Anderson's formula for narceïne, $C_{23}H_{29}NO_9 + 2H_2O$, which is the generally received one, requires modifying to $C_{23}H_{27}NO_8 + 3H_2O$. The hydrated compound melts at about 170°, and loses $2H_2O$ readily at 100°, the third mol. being expelled with greater difficulty; the anhydrous compound melts at 140—145°, is very hygroscopic, unites with 1 mol. H_2O when exposed to the air, and then melts above 160°. The base obtained by Roser by heating narcotine methiodide with alkali, and named by him pseudonarceïne (Abstr., 1888, 1316), is identical with narceïne. Assuming that the group CH_2O_2, in narcotine, occupies the same position as in hydrastine, narceïne may be represented as a substituted phenyl benzyl ketone,

$$\overset{3}{C}OOH \cdot C_6H_2\overset{1\,:\,2}{(OMe)_2} \cdot \overset{4}{C}O \cdot CH_2 \cdot \overset{1'}{C}_6H(CH_2 \cdot CH_2 \cdot NMe_2)\overset{2'}{(OMe)}\overset{3'\,or\,6'}{<}{}^{\overset{4'}{O}}_{\underset{5'}{O}}{>}CH_2.$$
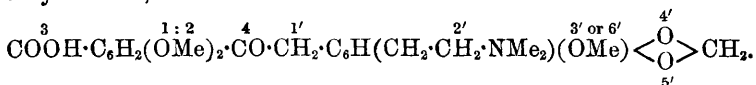
The alkaloïd thus contains no asymmetrical carbon atom; this is in accord with its optical inactivity. The above constitutional formula is fully in agreement with the behaviour of the alkali salts of the alkaloïd.

The *potassium* and *sodium* salts of narceïne are obtained by heating the base at 60—70° with 33 per cent. aqueous alkali; on adding ether to their alcoholic solutions, the salts are precipitated in crystals containing 1 mol. EtOH. The *potassium* salt melts at 90°, and the *sodium* salt at 159—160°. The alkaloïd is regenerated when the alkali salts are treated with acids or carbonic anhydride. Crude narceïne may be purified by means of the sodium salt. The *barium* salt melts at 182°, the *lead* salt at about 157°, and the *copper* salt decomposes at 172°.

Sodium narceïne gives with the undermentioned reagents the following compounds:—$C_{23}H_{26}EtNO_8$,MeI (m. p. 203°), with methylic iodide and ethylic alcohol; $C_{23}H_{26}MeNO_8$,MeI (m. p. 193—194°), with methylic iodide and methylic alcohol; $C_{23}H_{26}EtNO_8$,EtI (m. p. 131—132°), with ethylic iodide and ethylic alcohol; $C_{23}H_{26}MeNO_8$,EtI

(m. p. 203°), with ethylic iodide and methylic alcohol; $C_{23}H_{26}EtNO_8.C_2H_5I$ (m. p. 154—155°), with allylic iodide and ethylic alcohol; $C_{23}H_{26}MeNO_8,MeI$, with methylic iodide and ether. *Methylic narceïne* (see below) is obtained by boiling the sodium salt with methylic alcohol.

Narceïne hydrochloride crystallises with $5\frac{1}{2}H_2O$ and $3H_2O$; the anhydrous salt melts at 190—192°. The *platinochloride* crystallises with $2H_2O$, melts at 190—191°, and decomposes at 195—196°; the *nitrate* decomposes at 97°; the *sulphate* loses its water of crystallisation when kept in a partial vacuum.

Methylic narceïne forms a *hydrochloride* which crystallises from water in rectangular tables, and melts at 149°; the *platinochloride* melts at 205—206°; the *hydrobromide* melts at 148°; and the *hydriodide* melts at 139°. *Ethylic narceïne hydrochloride* melts at 206—207°; the *platinochloride* melts at 194—195°; the *hydrobromide* melts at 215—216°; and the *hydriodide* melts at 212°.

A determination by Zeisel's method established the presence of three methoxy-groups in narceïne. When narceïne is boiled with a solution of hydroxylamine hydrochloride, and ammonia is added to the product, the *oxime anhydride*, $C_{23}H_{26}N_2O_7$, is precipitated; it separates from alcohol in white crystals, melts at 171—172°, and forms a *hydrochloride* melting at 206—208°. When the anhydride is treated with potash, the *oxime*, $C_{23}H_{28}N_2O_8 + H_2O$, is obtained; it decomposes at 167°. The *phenylhydrazone hydrochloride*, $C_{29}H_{31}N_3O_6,HCl$, melts at about 175°, resolidifies above this temperature, and again melts at 215—220°. This modification of higher melting point is also obtained by crystallising the lower melting compound from hot absolute alcohol.

If narceïne is heated at 100° for three hours in a sealed tube, with excess of methylic iodide, a resinous mass is formed; when it is heated with potash, trimethylamine passes over, and the potassium salt of *narceonic acid*, $C_{21}H_{20}O_8$, remains in solution; the pure acid crystallises in white, lustrous, six-sided prisms, and melts at 208—209°.

The authors failed to obtain the additive compounds of narceïne with ethylic bromide and benzylic chloride, described by Claus and Ritzefeld (Abstr., 1885, 996). By oxidising narceïne with acid and alkaline permanganate, and also with nitric acid, hemipinic acid was obtained, but the formation of Claus and Meixner's narceïnic acid (Abstr., 1888, 612) was not observed. A. R. L.

Note by Abstractor.—Besides the derivatives of narceïne described in this abstract, in most cases the corresponding derivatives of the so-called pseudonarceïne were also prepared. Although the authors conclude that the compounds from both sources are identical, it is to be noticed that the melting points recorded of the derivatives of pseudonarceïne are distinctly higher than those from narceïne.

Action of Methylic Iodide on Papaverinic acid. By F. SCHRANZHOFER (*Monatsh.*, **14**, 521—535; compare Abstr., 1889, 1016).—When papaverinic acid, methylic iodide, and methylic

alcohol are heated together in sealed tubes at 100° for 18—19 hours, two products are obtained, one of which is readily soluble in acetone, whilst the other is only sparingly soluble. The latter the *methylbetaïne* of *papaverinic acid*, $C_{17}H_{15}NO_7 + H_2O$, when obtained free from iodine, crystallises in yellow, transparent plates, melts with decomposition at 192—194°, and dissolves in sodium carbonate solution with evolution of carbonic anhydride. It is a monobasic acid, forms crystalline *silver* and *barium salts*, and a *hydrochloride* crystallising in yellow prisms, and melting with decomposition at 182—184°. The *platinochloride*, $(C_{17}H_{15}NO_7)_2,H_2PtCl_6 + H_2O$, is not well characterised. That portion of the product above-mentioned which is soluble in acetone is resolved, on distillation, into two substances. Of these, one is the *methylic salt* of the *methylbetaïne* of *papaverinic acid*. $C_{18}H_{17}NO_7$; it crystallises in large, white plates, melts at 122—124°, and becomes rose-coloured on exposure to the light. The other is an isomeride of the betaïne, $C_{17}H_{15}NO_7$, described above ; it crystallises in white, microscopic needles, which are anhydrous, is insoluble in ether, sparingly soluble in water, melts at 195—197°, and appears, from an analysis of its barium salts, to be a bibasic acid.   G. T. M.

Hydrastine. By M. FREUND and F. LUTZE (*Ber.*, **26**, 2488—2490).—*Benzylhydrastine*, $C_{21}H_{20}NO_6 \cdot C_7H_7$, is prepared by warming the hydriodide (see below) with potash, and is deposited from alcohol in yellow crystals melting at 135°. The *hydrochloride*, $C_{28}H_{27}NO_6,HCl$, melts at 224°. The *hydrobromide*, $C_{28}H_{27}NO_6,HBr$, melts at 228°. The *nitrate* melts at 177°. The *hydriodide* is formed by the action of benzylic iodide on hydrastine in alcoholic solution; it crystallises from water, and melts at 177°. The *hydroxide*, $C_{21}H_{21}NO_6,C_7H_7 \cdot OH$, is obtained from the chloride by treatment with silver oxide, and is deposited in needles which contain water of crystallisation, and melt at 194°. *Benzylhydrastamide*, $C_{28}H_{30}N_2O_6$, is prepared from the hydriodide by the action of ammonia, and melts at 116°. By the action of mineral acids, or of concentrated alkalis on the amide, the imide, $C_{28}H_{28}N_2O_5$, is obtained in pale yellow crystals melting at 140°; its *hydrochloride* melts at 156° ; the *methiodide* and *ethiodide* are crystalline, and melt at 230° and 232° respectively. *Benzylhydrasteine*, $C_{28}H_{29}NO_7$, is prepared by boiling benzylhydrastine with concentrated potash, and crystallises from alcohol in colourless needles which melt at 159°. The *oxime anhydride*, $C_{28}H_{28}N_2O_6$, is formed by the action of aqueous hydroxylamine hydrochloride on the preceding compound, and crystallises from alcohol in pale yellow needles melting at 135°.

J. B. T.

Organic Chemistry.

Metallic Derivatives of Acetylene. By E. H. KEISER (*Amer. Chem. J.*, **15**, 535—539; compare Abstr., 1892, 1416).—When acetylene is passed into a solution of mercuric iodide in potassium chloride to which caustic potash has been added, a compound C_2Hg is precipitated in white flakes. This substance explodes violently when heated, dissolves in hydrochloric acid with evolution of acetylene, and, when treated with an alcoholic solution of iodine, yields di-iodo-acetylene, which polymerises, after a time, to crystals that melt at 187°; probably of hexiodobenzene.

When acetylene is passed into a saturated aqueous solution of mercuric chloride, a compound $C_2(HgCl)_2 + \frac{1}{2}H_2O$, is obtained as a granular, white precipitate. It explodes but feebly when heated, and does not dissolve in dilute hydrochloric acid. C. F. B.

Decomposition of Chloroform. By C. SCHACHT and E. BILTZ (*Pharm. J. Trans.*, **52**, 1005—1006).—Chloroform is not decomposed by the action of sunlight unless oxygen is present, when, in the first stages of the decomposition, chlorine is liberated, and this, acting on the alcohol contained in the chloroform, produces hydrogen chloride, which is then found instead of free chlorine. Hence the liberation of chlorine has been disputed by some who have over-looked the presence of alcohol in the chloroform operated on. Pure chloroform begins to decompose immediately in strong daylight, but the addition of alcohol prevents or arrests the decomposition, and will, moreover, on agitation of the liquid, remove any free chlorine and also any carbon oxychloride already liberated. The authors have found that the addition of 0·25 per cent. of alcohol suffices to preserve chloroform for at least a month in average daylight; 0·5 per cent. will preserve it for a year; and 1 per cent. for many years. The amount of alcohol in a sample may be inferred from the specific gravity, which at 15° is for pure chloroform, 1·5020; with 0·25 per cent. alcohol, 1·4977; with 0·5 per cent., 1·4939; with 1 per cent., 1·4854; with 2 per cent., 1·4705. R. R.

Isocyanogen Tetrabromide (Tetrabromoformalazine). By J. THIELE (*Ber.*, **26**, 2645—2647; compare Pulvermacher, this vol., i, 12).—Amidotetrazotic acid (Abstr., 1892, 1299) yields, on oxidation in alkaline solution, salts of azotetrazole, $\begin{smallmatrix}N-N\\ \| \quad\, \\ N\cdot NH\end{smallmatrix}{>}C\cdot N{:}N\cdot C{<}\begin{smallmatrix}N-N\\ \quad\, \|\\ NH\cdot N\end{smallmatrix}$ The hydrazotetrazole obtained by reducing the latter, when treated with bromine, furnishes isocyanogen tetrabromide (tetrabromoformalazine), $CBr_2{:}N{:}N{:}CBr_2$; this crystallises from glacial acetic acid in large, lustrous prisms, is insoluble in water, melts at 42°, and is readily volatile with steam, the warm vapour attacking the

mucous membrane. When warmed with concentrated sulphuric acid, carbonic anhydride and hydrogen bromide are evolved, and water precipitates hydrazine sulphate from the solution. The tetrabromide dissolves when gently warmed with alkalis, and hydrazine is only recognised in the solution after acidification; if the alkaline solution is distilled, the last fraction contains a compound which is, perhaps, isocyanogen oxide, CO:N·N:CO, or a polymeride. When an oxidisable substance is present, a strong odour recalling that of an isonitrile is recognised, which may be due to isocyanogen, C:N·N:C.

<div align="right">A. R. L.</div>

Action of Chlorine on Ethylic Alcohol. By M. ALTSCHUL and V. MEYER (*Ber.*, **26**, 2756—2759).—The authors have examined an oily liquid which is obtained as a bye-product in the manufacture of chloral by the action of chlorine on ethylic alcohol. The oil was separated from admixed chalk and calcium chloride by distillation with steam, and, on rectification, three fractions were obtained : the first portion (60—90°) consists largely of chloroform, which appears to be formed by the action of the steam on trichloracetic acid. The second fraction (90—140°) has not yet been investigated; the third (140—168°) consists of ethylic dichloracetate, trichlorethylic alcohol, and probably dichlorethylic alcohol. Ethylic dichloracetate was identified by the production of ethylic iodide and dichloracetamide; the trichlorethylic alcohol yields a metanitrobenzoate, $NO_2·C_6H_4·COO·C_2H_2Cl_3$, crystallising in transparent plates; it melts at 75°, and is identical with the compound prepared from pure trichlorethylic alcohol.

<div align="right">J. B. T.</div>

New Method of preparing Ethylic Ether and its Homologues. By F. KRAFFT (*Ber.*, **26**, 2829—2833).—In the preparation of ether by means of sulphuric acid, the latter compound undergoes a certain amount of reduction to sulphurous acid; this being due to the alcohol. In point of stability towards alcohol, the aromatic sulphonic acids are superior to sulphuric acid. The author shows (see also this vol., i, 91) that the aromatic sulphonic acids can be employed for the continuous etherification of alcohols in the same manner as sulphuric acid. Thus in the case of ethylic alcohol and benzenesulphonic acid :—$PhSO_2·OH + EtOH = PhSO_2·OEt + H_2O$; $PhSO_2·OEt + EtOH = PhSO_2·OH + Et_2O$; the alcohol is dropped on to the benzenesulphonic acid heated to about 140°. Methylic propylic ether was prepared by this method from a mixture of methylic and propylic alcohols ; it was found to boil at 36·6—37·4° (752 mm.), and its sp. gr. at 0° was 0·7460 (compare Henry, Abstr., 1892, 27).

<div align="right">A. R. L.</div>

Synthesis of Erythritol and of an Isomeride. By G. GRINER (*Compt. rend.*, **117**, 553—556).—The unstable liquid obtained by the action of bromine on erythrene at a low temperature (Abstr., 1893, i, 450) is the dibromide, $CH_2:CH·CHBr·CH_2Br$, which, when treated with bromine, yields the tetrabromide described by Ciamician and Magnaghi. It is isomeric with the solid dibromide,

<div align="center">$CH_2Br·CH:CH·CH_2Br$,</div>
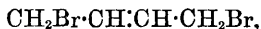
which served for the synthesis of erythritol (*loc. cit.*). When these dibromides are treated with a 1 per cent. aqueous solution of potassium permanganate in presence of alcohol at about 0°, the liquid dibromide yields a dibromhydrin melting at 135°, identical with that obtained by Champion by the action of hydrobromic acid on erythritol, and yielding a diacetin, $C_4H_6Br_2O_2Ac_2$, melting at 133—134°, whilst the solid dibromide yields a dibromhydrin melting at 83°, and a diacetin melting at 96°.

The dibromhydrins may be converted into tetracetins, but the process has the disadvantage of requiring somewhat high temperatures. It is more convenient to convert them into dioxides by the action of dry, solid potassium hydroxide at the ordinary temperature, the dioxides being afterwards converted into the corresponding tetrahydric alcohol by heating with water below 100°.

The liquid dibromide yields a dioxide which melts at 4°, and boils at 59—60°, under a pressure of 30 mm.; it is soluble in alcohol and water; sp. gr. at 16° = 1·113. When its aqueous solution is heated on a water-bath, it yields a compound $C_4H_{10}O_4$, crystallising from alcohol in small, silky tufts melting at 72°, very soluble in water, and even deliquescent; more soluble in alcohol than ordinary erythritol. This compound yields a tetracetin, $C_4H_6O_4Ac_4$, melting at 53°, and is an isomeride of ordinary erythritol.

The solid dibromide in like manner yields ordinary erythritol by conversion into a dioxide, and subsequent hydration of the latter (compare *loc. cit.*). C. H. B.

Iodide of Starch. By G. ROUVIER (*Compt. rend.*, **117**, 461).— Measured volumes of starch and iodine solutions of known strength were mixed together, and concentrated sodium chloride solution was added. After some time, the iodine in the precipitate and that remaining in solution was determined by means of thiosulphate solution. The quantity of iodine taken up by a given quantity of starch increases with the quantity of iodine solution added, until it reaches a maximum corresponding with the formula $(C_6H_{10}O_5)_{16}I_5$, beyond which no further combination takes place, even with a large excess of iodine.

With a given weight of iodine and starch, the quantity of iodine remaining uncombined increases with the volume of the liquid, provided that the proportion of iodine is not greatly in excess of that required to give a compound containing 19·6 per cent., or the maximum quantity, of iodine. If this proportion is exceeded, an increase in the total volume of the liquid does not prevent the formation of the compound $(C_6H_{10}O_5)_{16}I_5$ (compare Abstr., 1892, 578, 801, and 1171, and 1893, i, 683). C. H. B.

Chemistry of Plant Fibres : Celluloses, Oxycelluloses, and Lignocelluloses. By C. F. CROSS, E. J. BEVAN, and C. BEADLE (*Chem. News*, **68**, 225—227; also *Ber.*, **26**, 2520—2533).—Collating work done by them on jute fibre—the simplest type of lignification—the authors note that by chlorination this fibre yields 72 to 75 per cent. of α-cellulose, but, by treatment with dilute nitric acid, or by repeated

bromination, or by regulated oxidation with chromic acid, the yield of α-cellulose is 60—63 per cent. Moreover, the cellulose of jute fibre under hydrolysis with hydrochloric acid yields but traces of furfuraldehyde, whereas 6 per cent. of this aldehyde is obtained from it by means of a mixture of concentrated sulphuric acid and aqueous hydrochloric acid; under similar treatment, more resistant celluloses, such as cotton cellulose, yield only a few tenths per cent., unless they have been previously subjected to oxidation, then the yield of furfuraldehyde may attain 8 per cent.; it seems, therefore, that jute fibre cellulose is an oxycellulose; and, in addition, about one-sixth of the cellulose obtained by chlorination consists of β-cellulose containing two methoxyl-groups in the formula weight, $C_{19}H_{22}O_{10}$.

The non-celluloses, either in the raw fibre or in the chlorinated fibre, give over 9 per cent. of furfuraldehyde when boiled with hydrochloric acid; they also contain over 14 per cent. of methoxyl, and when rendered soluble by chlorination, yield quinone chlorides corresponding to 7—9 per cent. (on the fibre substance) of keto-R-hexene derivatives; these derivatives are assumed to contain groups of the general form $CO{<}^{CH == CH}_{C(OH)_2 \cdot C(OH)_2}{>}CH_2$, condensed by union of OH groups. The remaining portion of the non-celluloses consists of the complex $C_{13}H_{16}O_6$. Jute fibre is therefore regarded as consisting of 60—65 per cent. of α-cellulose, 15—20 per cent. of β-cellulose, 7—9 per cent. of keto-R-hexene derivatives, and 18—22 per cent. of the above complex, and these substances appear to be so related chemically as to suggest a series of transitions from one extreme member to the other.

Incidentally it is noted that, according to the authors' views, the production of furfuraldehyde does not depend on the presence of a pentaglucose. D. A. L.

Preparation of Methylamine: Constitution of Hexamethylenetetramine. By A. TRILLAT and FAYOLLAT (*Compt. rend.*, 117, 628—630).—100 grams of a 33 per cent. solution of formaldehyde is mixed with a cold aqueous solution of ammonia until there is no further development of heat, 200 grams of zinc powder is added to the mixture all at once, and then 750 grams of ordinary hydrochloric acid very gradually, the operation occupying from eight to ten hours. The product is now mixed with a large excess of sodium hydroxide, and distilled in a current of steam, the distillate being received in dilute hydrochloric acid; ammonia passes over first, and methylamine afterwards, the two hydrochlorides being separated by means of alcohol, after evaporating to dryness. The methylamine thus obtained is free from secondary and tertiary amines.

It would seem that the action of ammonia on formaldehyde yields the compound $CH_2(N{:}CH_2)_2$, and the latter is then reduced, yielding $CH_2(NHMe)_2$, which, by the action of water, is converted into formaldehyde and methylamine.

The authors consider that the constitution of the product of the action of ammonia on formaldehyde is more probably $CH_2(N{:}CH_2)_2$ than $N_4(CH_2)_6$. The first product of the reaction may be methylene-

amine, $CH_2:NH$, which reacts with a further quantity of aldehyde, $2CH_2:NH + CH_2O = CH_2(N:CH_2)_2 + H_2O$. It is known that, with formaldehyde, aniline yields the compound $CH_2:NPh$, whilst monomethylaniline gives the compound $CH_2(NPhMe)_2$. C. H. B.

Nitrites of Amines. By W. A. NOYES (*Amer. Chem. J.*, **15,** 539—546).—The nitrites of some amines of the type $CHR_2 \cdot NH_2$ have been prepared, and found to be stable at the ordinary temperature; they are, however, decomposed, with evolution of nitrogen, when their solutions are boiled or evaporated to dryness. The amines were in general prepared by reducing the corresponding ketoximes.

Diethylcarbinamine, $CHEt_2 \cdot NH_2$, is a colourless liquid boiling at 89—91°, of sp. gr. 0·7487 at 20°/4°; the *hydrochloride* crystallises in needles melting at 216—217°; the *platinochloride* in needles; and the *nitrite* in deliquescent, white needles. *Dipropylcarbinamine,* $CHPr_2" \cdot NH_2$, is a colourless liquid, boils at 139—140°, and has a sp. gr. 0·7667 at 20°/4°. The *hydrochloride* crystallises in needles melting at 241—242°; the *platinochloride* in pale yellow scales; the *nitrite* is decomposed by boiling, much more rapidly in concentrated than in dilute solution. *Di-isobutylcarbinamine* is a colourless liquid, boils at 166—167°, and has the sp. gr. 0·772 at 20°/4°. The *hydrochloride* crystallises in needles melting at 247—248°; the *platinochloride* in pale yellow needles; the *carbonate* and the *nitrite* in white needles. Hexamethylenediamine nitrite is only partially decomposed when its aqueous solution is boiled. Dihydromesoanthramine nitrite yields anthracene. *Diphenylcarbinamine nitrite,* which crystallises in white needles, yields diphenylcarbinol. C. F. B.

Action of Sodium on Acetone. By P. C. FREER (*Amer. Chem. J.*, **15,** 582—605).—It is proved that when metallic sodium acts on a dilute xylene solution of acetone (1 : 100), hydrogen is evolved to the extent of about 63 per cent. of the amount corresponding with the displacement of 1 atom of hydrogen by sodium. When sodium acts on pure acetone, none of this hydrogen is evolved; it is used up in reducing the acetone to isopropylic alcohol, &c.

Acetone in ethereal solution was then exposed to the action of sodium, this and other operations being carried out in an atmosphere of hydrogen. The product consisted of two parts, nearly equal in amount, and respectively insoluble and soluble in ether. The former was found to consist chiefly of acetone sodium, together with sodium isopropoxide and disodium pinaconate in about equal proportions, and a trace of sodium ethoxide. The part soluble in ether consists almost entirely of sodium acetone. *Sodium acetone* oxidises very readily, and is decomposed by cooled dilute acetic acid, yielding acetone, together with small quantities of mesitylic oxide and phorone. It appears to have the formula $CH_2:CMe \cdot ONa$ (and not $CH_2Na \cdot COMe$), because, when it is treated with benzoic chloride, β-allylic benzoate, $CH_2:CMe \cdot OBz$, is among the products. The product of the action is extracted successively with sodium hydrogen carbonate, carbonate, and hydroxide. The residual oil contains mesitylic oxide and ethylic, isopropylic, and β-allylic benzoates; when hydrolysed with

dilute hydrochloric acid, it yields benzoic acid, together with ethylic and isopropylic alcohols and acetone; with caustic potash, no acetone is obtained, but phorone and mesitylic oxide instead. The portion soluble in sodium hydrogen carbonate contains benzoic acid. That soluble in sodium carbonate contains mono- and di-benzoylacetone, and yields acetophenone, acetic acid, and benzoic acid when distilled. The higher-boiling part of the insoluble oil contains some substances which have been isolated, but not yet identified.

C. F. B.

Electrical Conductivity of Formic acid. By V. SAPOJNIKOFF (*J. Russ. Chem. Soc.*, **25**, 109—110).—As a rule, pure substances are bad conductors of electricity, but Hartwig found that formic acid conducted comparatively well. The author has repeated the experiments with as pure acid as he could obtain (m. p. 8·39°), and finds for it a conductivity only one-sixteenth of that observed by Hartwig. As this acid still contained about 0·2 per cent. of water, he is of opinion that the pure acid is practically a non-conductor.

J. W.

Oxymethylene Derivatives of Ethylic Acetoacetate, Acetylacetone, and Ethylic Malonate. By L. CLAISEN (*Ber.*, **26**, 2729—2735).—When ethylic acetoacetate, or acetylacetone is heated in a reflux apparatus with ethylic orthoformate and acetic anhydride, alcohol is eliminated and ethoxymethylene derivatives are obtained. A similar condensation occurs with ethylic malonate, but the action is much slower and requires the addition of zinc chloride.

Ethylic ethoxymethyleneacetoacetate, OEt·CH:CAc·COOEt, is a colourless oil, boils at 265—266° under ordinary pressure, and at 149—150° under 15 mm., and has a sp. gr. of 1·0736 at 15°. It combines with phenylhydrazine to form ethylic phenylmethylpyrazolecarboxylate, which melts at 53°. When treated with water or alcohol, it yields *ethylic hydroxymethyleneacetoacetate.* This is a colourless liquid, boils at 199—200° under the ordinary pressure, and at 95° under 21 mm. pressure, has a sp. gr. of 1·141 at 15°, is soluble in dilute alkali carbonates, and reddens litmus paper. With copper acetate, it yields a blue, crystalline copper salt.

Ethoxymethyleneacetylacetone, $C_5H_6O_2$:CH·OEt, boils at 256—258° under the ordinary pressure, and at 141° under 16 mm. pressure. *Hydroxymethyleneacetylacetone* melts at 47°, boils at 190—200° under the ordinary pressure, and at 100° under 20 mm. pressure, and is a stronger acid than ethylic hydroxymethyleneacetoacetate.

Ethylic ethoxymethylenemalonate, OEt·CH:C(COOEt)₂, is a colourless oil, boils at 280°, has a sp. gr. of 1·0855 at 15°, and is not decomposed by water at the ordinary temperature.

When ethylic acetoacetate and ethylic orthoformate are allowed to remain in contact with acetic chloride instead of being heated with acetic anhydride, a different reaction takes place, and ethylic acetate, ethylic formate, and ethylic ethoxycrotonate, OEt·CMe:CH·COOEt, are formed. The latter melts at 31°, boils at 199—200°, and, when distilled over calcium hydroxide, yields the alcohol CH_2:CMe·OH, which boils at 62°.

Compounds containing the methenyl group CH combined with two

residues of the group ·CO·CH₂·CO· are obtained by the prolonged action of ethylic orthoformate and acetic anhydride on an excess of ethylic acetoacetate or acetylacetone. These *methenyl* compounds are more easily obtained by adding the alkali salts of ethylic acetoacetate or acetylacetone to an alcoholic solution of the ethoxymethylene derivatives described above. *Diethylic methenyldiacetoacetate,* $C_6H_8O_3$:$CH·C_6H_9O_3$, melts at 96°. *Methenyldiacetylacetone,*

$$C_5H_6O_2\text{:}CH\text{·}C_5H_7O_2,$$

melts at 115°, and, by the withdrawal of the elements of water, yields a crystalline compound, $C_{11}H_{12}O_3$, which melts at 112°. When these methenyl compounds are treated with ammonia, they yield pyridine derivatives. Thus, diethylic methenyldiacetoacetate, when heated with ammonium acetate, yields ethylic dimethylpyridinedicarboxylate, and methenyldiacetylacetone, when allowed to remain in ammoniacal solution, yields $\alpha\alpha'$-diacetyllutidine (m. p. 73—74°). In many cases it is unnecessary to prepare the methenyl compound; thus, ethylic dimethylpyridinedicarboxylate is obtained by heating ethylic ethoxymethyleneacetoacetate with ethylic paramidoacetoacetate.

E. C. R.

Derivatives of Diethylic Succinosuccinate. By N. KIJNER (*J. Russ. Chem. Soc.*, **25**, 125—132).—Succinosuccinic acid (1 gram) was heated for six hours at 225° with hydriodic acid (15 c.c.) of sp. gr. 1·96. No hexamethylene was obtained, but a liquid boiling from 200° to 220°. Diketohexamethylene gave similar results.

Phosphorus pentachloride with diketohexamethylene in cold chloroform solution gives crystals which melt at 125·5° and have the composition $C_6H_8Cl_4$. These sublime in needles at a temperature below their melting point, and may be recrystallised from boiling alcohol. Paradichlorobenzene is formed at the same time.

When the sodium compound of diethylic succinosuccinate is boiled with ethylic chloro-formate, a substance $C_{12}H_{14}O_6(COOEt)_2$ is formed, which is easily soluble in chloroform, less soluble in alcohol, and melts at 127°. It does not dissolve in alkalis, does not fluoresce, and its alcoholic solution does not colour ferric chloride. When treated with bromine, it loses 2 atoms of hydrogen, giving a compound $C_{12}H_{12}O_6(COOEt)_2$, melting at 129°; this may also be made from the sodium salt of diethylic quinonehydrodicarboxylate, by treating it with ethylic chloro-formate. J. W.

Action of Iodic acid on Acetonedicarboxylic acid. By A. ANGELI and E. LEVI (*Gazzetta*, **23**, ii, 97—100).—On treating acetonedicarboxylic acid with aqueous iodic acid, carbonic anhydride is evolved and heat is developed. The mixture is kept cool, and, after a time, *tetriodoacetone*, $CO(CHI_2)_2$, is deposited; it crystallises in beautiful, yellow needles, melting at 142° with decomposition. It is very soluble in acetone, less so in benzene, alcohol, ethylic acetate, or chloroform, but its solutions soon become coloured, owing to liberation of iodine. On distillation with hydriodic acid and a little red phosphorus, it yields acetone, iodoform, and symmetrical diiodoacetone,

but it gives no appreciable quantity of iodoform when treated with alkali carbonates.　　　　　　　　　　　　　　　　　　　W. J. P.

Barium Antimony Tartrate. By E. MAUMENÉ (*Compt. rend.*, **117**, 666—668).—The numbers obtained by Dumas and Piria, in their analyses of barium antimony tartrate, did not agree well with those calculated from the formula, and they attributed the divergences to the retention of water and the absorption of carbonic anhydride. The author points out that, according to his general laws, the formula of the salt is $C_8H_{7\cdot79}O_{13\cdot79}(SbO_3)_{1\cdot17}(BaO)_{1\cdot07}$, and that the numbers calculated from this formula ($O = 8$, $C = 6$, &c.) agree closely with the results of analysis.　　　　　　　　　　　　　　　　C. H. B.

Methylic Tartrates and Ethylic Tartrates. By J. FAYOLLAT (*Compt. rend.*, **117**, 630—633).—Lithium, sodium, potassium, and ammonium methylic tartrates, and lithium, sodium, potassium, barium, and calcium ethylic tartrates, all crystallise in anhydrous crystals. Ammonium methylic tartrate crystallises with some difficulty, and is very hygroscopic. Polarimetric observations with (1) tartaric acid, (2) methylic hydrogen tartrate, (3) lithium methylic tartrate, (4) ammonium methylic tartrate, (5) sodium methylic tartrate, (6) potassium methylic tartrate, (7) ethylic hydrogen tartrate, (8) lithium éthylic tartrate, (9) sodium ethylic tartrate, (10) potassium ethylic tartrate, in aqueous solutions containing 1 gram molecule in 8000 c.c. of water, gave the following results.

	1.	2.	3.	4.	5.	6.
Observed deviation, column 20 cm. long	+ 0·61	0·75	1·14	1·28	0·99	1·16
Specific rotatory power	+16·1	18·1	26·5	28·0	21·0	22·7

	7.	8.	9.	10.
Observed deviation, column 20 cm. long	0·98	1·34	1·39	1·40
Specific rotatory power	21·8	28·8	27·5	21·6

It will be observed that, in each series, the deviations produced by the alkali salts are very approximately equal, which indicates a degree of dissociation practically the same for the various salts in the same series. Calcium and barium ethylic tartrates were examined in solutions containing 1 gram molecule in 16 litres, the deviations being +1·21 and +1·26, and the specific rotatory powers +24·3 and +20·3 respectively.

The solubilities of the salts in alcohol are so small that no comparative observations are possible, but the results with saturated solutions show that both the methylic tartrates and the ethylic tartrates retain their dextrogyrate character.　　　　　　　　　　C. H. B.

. Influence of Organic Solvents on Specific Rotatory Power. By P. FREUNDLER (*Compt. rend.*, **117**, 556—559).—The author has measured the specific rotatory power of propylic diacetyltartrate, dipropionyltartrate, dibutyryltartrate, di-*n*-valeryltartrate, and di-*n*-

caproyltartrate, dissolved in ether, alcohol, acetone, butyl ketone, light petroleum, carbon bisulphide, methylic alcohol, toluene, benzene, methylenic chloride, chloroform, carbon tetrachloride, ethylenic chloride, ethylidenic chloride, chlorethylidenic chloride, methylenic bromide, bromoform, ethylenic bromide, propylic bromide, and methylic iodide. The results show that the nature of the solvent exerts very considerable influence on the rotatory power of the dissolved substances. The value of $[\alpha]_D$ for propylic diacetyltartrate, for example, varies from $+36.7°$ in carbon bisulphide to $-2.6°$ in bromoform, the specific rotatory power of the compound itself being $+13.4°$. Similarly, the value for the di-n-valeryltartrate varies from $+8.2°$ in acetone to $-4.7°$ in bromoform, the value for the salt itself being $+6.7°$. On the whole, oxygen compounds have little influence, whilst haloïd derivatives and compounds of the benzene series tend to reduce the value of $[\alpha]_D$, and even to change its sign. The effect of different solvents is of the same order with all five compounds.

The changes in rotatory power may be due to (1) polymerisation of the active molecules, or (2) combination of the active substance with the solvent. Salts of the alkaloïds, for instance, are known to combine with alcohols and with benzene, and propylic tartrate forms compounds with benzene. Cryometric measurements show that in solutions in ethylenic bromide which have normal rotatory power, the molecular weight is normal; but in solutions in benzene which have much lower rotatory power, the molecular weight is considerably below the calculated value. It would seem that some change of the nature of dissociation takes place.

C. H. B.

Thiocarbamides. By H. SALKOWSKI (*Ber.*, **26**, 2923).—The paper criticised by the author (this vol., i, 11) was by G. Mazzaron, not by G. Mazzara.

J. B. T.

Some Nitrogen Derivatives of the Higher Fatty Acids. By P. EITNER and H. WETZ (*Ber.*, **26**, 2840—2847).—The amides of the higher fatty acids can be distilled under diminished pressure almost without decomposition, whilst that of the bibasic sebacic acid is almost completely decomposed. Lauramide boils at 199—200° (12·5 mm.), myristamide at 217° (12 mm.), palmitamide at 235—236°, and stearamide at 250—251° with slight decomposition, under the same pressure.

The nitriles obtained from these amides have been employed for the preparation of several classes of derivatives. The imido-ethers are prepared by the action of dry hydrogen chloride on a liquid mixture of the nitrile with a molecule of isobutylic alcohol. *Laurimidoisobutyl ether hydrochloride*, $C_{16}H_{33}ON,HCl$, is a very hygroscopic, white, microcrystalline powder melting at 65—66°; it is slightly soluble in ether, readily in alcohol; in aqueous solution it soon undergoes decomposition. *Myristimidoiso-butyl ether hydrochloride*, $C_{18}H_{37}ON,HCl$, has similar properties, and melts at 69—70°. *Palmitimidoisobutyl ether hydrochloride*, $C_{20}H_{41}ON,HCl$, is less soluble and less hygroscopic than the above; it melts at 73°. *Stearimidoisobutyl ether hydrochloride*, $C_{22}H_{45}ON,HCl$,

is only slightly hygroscopic, and melts at 77—78°. It is also less soluble in ether than its lower homologues. *Sebacimidoisobutyl ether hydrochloride*, $C_{18}H_{36}O_2N_2,2HCl$, closely resembles the foregoing compound; it melts at 135° with decomposition.

From the imidoisobutyl ethers the corresponding amidine hydrochlorides may be prepared by the action of alcoholic ammonia. These compounds form fine, white plates or thin prisms, with a splendid silky lustre, and are not in the least degree hygroscopic. They form platinochlorides which crystallise from alcohol in slender, yellow needles. *Lauramidine hydrochloride*, $C_{12}H_{26}N_2,HCl$, melts at 128—129°; it is readily soluble in alcohol, slightly in water, insoluble in ether. *Myristamidine hydrochloride* is only very slightly soluble in water, and melts without decomposition at 135°. *Palmitamidine hydrochloride* is also scarcely soluble in water; it softens at 136°, and melts at 217°. Stearamidine hydrochloride has been previously prepared by Pinner (*Die Imidoäther und ihre Derivate*, S. 130). *Sebacamidine hydrochloride* melts at 166—167°.

Palmitamidine, $C_{16}H_{34}N_2$, prepared by the action of sodium ethoxide on an alcoholic solution of the hydrochloride, crystallises from alcohol in lustrous plates melting at 85°. It distils almost without decomposition at 194° (13 mm.).

The amidoximes corresponding with the nitriles are prepared by the usual method, and resemble one another very closely. They form white, lustrous plates or broad prisms, with a faint pink or greenish surface lustre. They are insoluble in water, very slightly soluble in ether, readily in alcohol. *Lauramidoxime* melts at 92—92·5°, *myristamidoxime* at 97°, *palmitamidoxime* at 101·5—102°, and *stearamidoxime* at 106—106·5°. It was found impossible to prepare the amidoxime of sebacic acid.

The amidoximes unite with a molecule of sulphurous anhydride when this gas is passed through their solutions in benzene. The products formed cannot be distinguished from one another by appearance. They are white, crystalline powders which decompose slowly, with loss of sulphurous anhydride; they all liquefy at about 100°, and simultaneously decompose. The derivative of palmitamidoxime was converted into an *ammonium salt* by the action of dry ammonia gas; it is likewise a white, crystalline powder which decomposes in the air. These acids have the general formula $NH_2 \cdot CR \cdot N \cdot O \cdot SO_2H$, and the authors propose to call them *amidoxime-sulphurous acids*.

The nitriles of the monobasic acids readily unite with hydrogen bromide. The following compounds of this class were obtained.

	M. p.
Dilauronitrile hydrobromide, $(C_{12}H_{23}N)_2,HBr$ ..	75·5—76·0°
Dimyristonitrile hydrobromide, $(C_{14}H_{27}N)_2,HBr$	79·5—80·5
Dipalmitonitrile hydrobromide, $(C_{16}H_{31}N)_2,HBr$	84·0—85·0
Distearonitrile hydrobromide, $(C_{18}H_{35}N)_2,HBr$ ..	88·5—89·5

All these substances crystallise in colourless, narrow plates, are almost insoluble in water, readily soluble in alcohol, &c., and are not hygroscopic.   A. H.

Action of Ammonia on Ethylic 6-Ethoxycoumalin-3 : 5-dicarboxylate in absence of Water. By M. GUTHZEIT (*Ber.*, 26, 2795—2808).—The compound $CH \ll^{CH:CH}_{CH \cdot CO} > O$ is named by v. Pechmann (Abstr., 1891, 1460) coumalin instead of α-pyrone; the author also adopts this name. It has already been shown (Abstr., 1891, 939) that when ethylic ethoxycoumalindicarboxylate is shaken with dilute aqueous ammonia, ethylic ethoxyhydroxypyridindicarboxylate is formed. If dry ammonia is passed into a solution of ethylic ethoxycoumalindicarboxylate in benzene, a *substance*, $C_{11}H_{13}NO_6$, isomeric with that previously described (*loc. cit.*) is precipitated. When crystallised from a boiling mixture of acetone and alcohol, it forms a bright yellow powder, becomes red at 180°, melts at 199°, and yields $\alpha\alpha$-dichlorodinicotinic acid (m. p. 75—76°) on treatment with phosphorus pentachloride.

When the substance melting at 199° is treated with cold dilute aqueous sodium hydroxide, or when a hot aqueous solution of it, mixed with a little alcohol, is filtered into hot aqueous sodium carbonate, a sparingly soluble *sodium* salt, $C_{11}H_{12}NO_6Na + \frac{1}{2}H_2O$, is obtained, together with a bitter oil. It was noticed that the longer the substance of melting point 199° is boiled with water, previously to adding the solution to sodium carbonate, the more sodium salt is obtained. The compound obtained from the sodium salt by treating it with acids melts at 199°, but, unlike the original substance, does not become suddenly red at 180°. It therefore seemed probable that the original substance underwent isomeric change on heating. To put this to the test, the crude substance from ammonia and ethylic ethoxycoumalindicarboxylate was crystallised from a large quantity of cold acetone, when a white, flocculent compound, having the same composition as the original substance, was obtained; on heating this in a capillary tube in the ordinary way, it becomes red at 180° and melts at 199°, but if the capillary tube is introduced into a sulphuric acid bath, heated to 178—179°, the compound melts to a red liquid, almost immediately resolidifies, and melts a second time at 199°. The compound melting at 178—179° gives a yellow coloration with ferric chloride, and is very sparingly soluble in solvents, so much so that its molecular weight could not be determined by the cryoscopic method. Cold dilute alkalis dissolve it, forming a yellow solution, which, on acidification, evolves carbonic anhydride and deposits an oil; hot dilute alkalis produce the same effect, but partially convert the compound into the already mentioned sodium salt of the isomeride; whilst boiling with concentrated alkalis causes the evolution of ammonia. When either the crude substance (m. p. 199°) obtained from a boiling mixture of acetone and alcohol, or the compound prepared from the sodium salt, is recrystallised from cold acetone, an *isomeride* is obtained in the form of concentrically arranged prisms; it gradually becomes yellow when heated, melts sharply at 199°, gives a deep violet coloration with ferric chloride, is more soluble in solvents than the lower-melting isomeride, yields the sodium salt when treated with hot or cold dilute alkalis, and evolves only traces of ammonia when boiled with concentrated alkalis; a

molecular weight determination by the cryoscopic method established the formula $C_{11}H_{13}NO_6$. The *silver* salt is obtained as a white precipitate, stable towards light, when silver nitrate is added to a solution of the sodium salt; when heated with ethylic iodide, ethylic α-ethoxy-α-hydroxydinicotinate (m. p. 182°) is formed.

From these facts, it appears probable that the compound melting at 178—179° has the constitution $CH{\displaystyle\Big\langle}{\substack{CH(COOEt)\cdot CO\\ C(COOEt)-CO}}{\displaystyle\Big\rangle}NH$;

whilst that melting at 199° has the tautomeric formula

$$CH{\displaystyle\Big\langle}{\substack{CH(COOEt)-CO\\ C(COOEt)\cdot C(OH)}}{\displaystyle\Big\rangle}N.$$
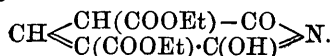
A. R. L.

Electrolytic Reduction of Aromatic Nitro-compounds. By L. GATTERMANN and K. KOPPERT (*Ber.*, **26**, 2810—2812).—A compound was obtained by the electrolytic reduction of paranitrotoluene (Abstr., 1893, i, 567), which was supposed to be nitramidorthobenzyltoluene. When this compound is reduced to the diamine, the latter converted into the hydrazine, and oxidised with copper sulphate, a hydrocarbon is obtained having the same boiling point (275—280°) as orthobenzyltoluene.

When a mixture of paranitrobenzylic alcohol (or its acetate), paranitrotoluene, and concentrated sulphuric acid is heated at 120—130°, *dinitrobenzyltoluene*, $NO_2\cdot C_6H_3Me\cdot CH_2\cdot C_6H_4\cdot NO_2$, is formed; it crystallises in yellow needles, melts at 137—138°, and is converted into the diamine on reduction with stannous chloride. The dihydroxy-compound obtained from this diamine is identical with that previously described (*loc. cit.*). A compound identical with the nitramidobenzyltoluene (*loc. cit.*) is obtained by heating together, at 160—170°, paramidobenzylic alcohol, paranitrotoluene, and concentrated sulphuric acid. These experiments, therefore, justify the assumption that, by the electrolytic reduction of paranitrotoluene, paratolylhydroxylamine is first formed, and then undergoes isomeric change into paramidobenzylic alcohol, the latter condensing with more paranitrotoluene. A. R. L.

Action of Nitrous acid on Anethoïl. By G. BOERIS (*Gazzetta*, **23**, ii, 165—194).—*Diisonitrosoanethoïl peroxide,*

$$\underset{N\cdot O\cdot O\cdot N}{OMe\cdot C_6H_4\cdot\overset{\displaystyle C}{\underset{\displaystyle \|}{}}\text{———}\overset{\displaystyle C}{\underset{\displaystyle \|}{}}Me},$$
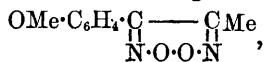
is prepared by the action of sodium nitrite on anethoïl in acetic acid solution; it crystallises in yellow needles melting at about 97°, and was prepared by Toennies (Abstr., 1881, 167) who assigned to it a constitution differing from the above. No isomeric modification seems to exist. The *mononitro*-derivative, $C_{10}H_9N_3O_5$, obtained by direct nitration, forms lustrous, yellow needles melting at 88—89°. The *bromo*-derivative, $C_{10}H_9BrN_2O_3$, was also prepared.

α-*Diisonitrosoanethoïl*, $OMe\cdot C_6H_4\cdot C(NOH)\cdot CMe\colon NOH$, obtained by reducing the peroxide with zinc-dust and acetic acid, crystallises in small, lustrous prisms melting at 125°; potassium ferricyanide reconverts it into the peroxide. Its *diacetyl* derivative, $C_{10}H_{10}N_2O_3Ac_2$,

forms needles melting at 89°; when dissolved in alcohol or potash, it slowly changes into diisonitrosoanethoïl anhydride.

β-*Diisonitrosoanethoïl* is obtained by heating the α-isomeride at 125°; it melts at 206° with decomposition, and further differs from the α-compound by being very sparingly soluble in alcohol. Its *diacetyl* derivative forms white needles melting at 104°, and, on treatment with potash or boiling with alcohol, is reconverted into the β-dioxime; the latter is converted into the peroxide by potassium ferricyanide.

Diisonitrosoanethoïl anhydride, $\mathrm{OMe \cdot C_6H_4 \cdot C{:}N}\!\!\!\diagup^{\mathrm{C{:}N}}_{}\!\!\!> O$, prepared by reducing the peroxide with tin and hydrochloric acid, crystallises in long, white needles melting at 63°; it is soluble in alcohol or benzene, and has the normal molecular weight in freezing benzene. The *mononitro*-derivative is obtained by direct nitration, and forms small, lustrous crystals melting at 98—99°. The *bromo*-derivative is fairly soluble in alcohol, and crystallises in small needles melting at 73—74°.

α-*Diisonitrosobromanethoïl,* $\mathrm{OMe \cdot C_6H_3Br \cdot C(NOH) \cdot CMe{:}NOH}$, is prepared by reducing the bromo-derivative of the anhydride with zinc-dust and acetic acid; it crystallises in very lustrous, small prisms melting at 143—144°. On heating with acetic anhydride, it yields a *diacetyl* derivative which forms thin needles melting at 101—102°, and soon decomposes in alcoholic solution, giving the bromo-derivative melting at 73—74° described above. The latter is also obtained on oxidising α-diisonitrosobromanethoïl with alkaline ferricyanide.

β-*Diisonitrosobromanethoïl* is prepared by heating the α-isomeride above its melting point; it forms small, white scales melting at 190°, and yields the peroxide on oxidation with alkaline ferricyanide. The *diacetyl* derivative is obtained in white needles melting at 130—131°. On reducing the β-dioxime with tin and hydrochloric acid, the same anhydride is obtained as by direct bromination of diisonitrosoanethoïl anhydride.　　　　　　　　　　　　　　　　　　　　　　W. J. P.

Synthesis of Ethers and Ketones from Phenols. By S. K. Dzerzgovsky (*J. Russ. Chem. Soc.*, **25**, 154—163).

—Catechol and chloracetic acid in molecular proportion are melted together, and to the product phosphorus oxychloride is added in quantity equal to the weight of the chloracetic acid taken. The mixture is heated until brown and syrupy, and then treated with three times its volume of water, from which, on cooling, crystals of the chloroketone,

$$\mathrm{C_6H_3(OH)_2 \cdot CO \cdot CH_2Cl,}$$
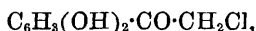
separate. The yield is 80 per cent. of the theoretical. The chloroketone crystallises in colourless prisms with $1\mathrm{H_2O}$, which is given off at 110°, and melts at 173°. It is easily soluble in alcohol, chloroform, ether, benzene, and carbon bisulphide. The aqueous solution is coloured green by ferric chloride, changing to purple on the addition of sodium carbonate. It reduces silver but not cupric salts, and has an acid reaction. The diacetate is insoluble in water, but crystallises

from aqueous acetic acid in pearly scales melting at 95°. It is soluble in alcohol, ether, and chloroform. On reduction with zinc and hydrochloric acid, the chloroketone gives a theoretical yield of *aceto-catechone*, $C_6H_3(OH)_2 \cdot COMe$, which crystallises in nodular aggregates of prismatic needles. These crystals contain no water of crystallisation, melt at 116°, and are easily soluble in most solvents. The diacetate crystallises from acetic acid in colourless plates melting at 87°.

Bromacetocatechone, $C_6H_3(OH)_2 \cdot CO \cdot CH_2Br$, crystallises with $1H_2O$, and melts at 167°.

α-Chloropropiocatechone, $C_6H_3(OH)_2 \cdot CO \cdot CHCl \cdot CH_3$, crystallises in prisms without water of crystallisation, and melts at 120°; the corresponding bromo-derivative melts at 141°.

β-Bromobutyrocatechone, $C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot CHBr \cdot CH_3$, is formed in an analogous manner, but the reaction in this case is hastened by the addition of zinc chloride. It crystallises in colourless prisms without water, and melts at 135°.

Guaiacol and quinol do not give ketones when treated with chloracetic acid and phosphorus oxychloride, but simply chloracetates. The chloracetate of guaiacol, $OMe \cdot C_6H_4 \cdot O \cdot CO \cdot CH_2Cl$, melts at 50°, and boils at 258—259°. The dichloracetate of quinol, $C_6H_4(O \cdot CO \cdot CH_2Cl)_2$, melts at 123°, and boils above 300°.   J. W.

Desmotropy in Phenols : Constitution of Tetrethylphloro-glucinol. By J. HERZIG and S. ZEISEL (*Monatsh.*, **14**, 376—381).—When dibromotetrethylphloroglucinol (Abstr., 1890, 243) is submitted to alkaline hydrolysis, it is converted into symmetrical tetrethylacetone, monobromotetrethylphloroglucinol, and oxalic acid, with elimination of bromine and carbonic acid. The constitution of the dibromo-compound is, therefore, probably represented by the formula

$$CO \Big\langle {}^{CEt_2 \cdot CO}_{CBr_2 \cdot CO} \Big\rangle CEt_2,$$
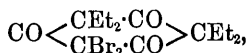
and that of the phenol by the formula $CO \Big\langle {}^{CEt_2—CO}_{CH:C(OH)} \Big\rangle CEt_2.$ The intermediate products may be either the unstable ketonic acid $CHBr_2 \cdot CO \cdot CEt_2 \cdot CO \cdot CEt_2 \cdot COOH$, or tetrethylacetone and dibromomalonic acid. In either case, dibromacetic acid is formed, and this, in the presence of alkali, is immediately hydrolysed into glyoxylic acid. The latter then reduces the dibromotetrethylphloroglucinol to the monobromo-compound, and is itself oxidised to oxalic acid in the process.

The dibromotetrethylphloroglucinol (14·58 grams) is boiled for an hour in a reflux apparatus with an aqueous solution of sodium hydroxide and carbonate (8·86 and 0·25 grams in 100 c.c.) in an atmosphere free from carbonic anhydride. The product consists of a colourless, oily layer floating on a yellow, aqueous layer. The oily layer is separated and purified, and a further portion distilled from the aqueous layer. It consists almost entirely of symmetrical tetrethylacetone (Abstr., 1892, 1188), boiling at 204·9—205·9° under a pressure of 738·5 mm. The carbonic acid was estimated in a portion

of the aqueous layer, and the monobromotetrethylphloroglucinol pre-
cipitated by hydrochloric acid from the remainder, the oxalic acid
being estimated in the filtrate. The monobromo-compound may be
reconverted into the dibromo-compound and worked up again until the
quantity is too small for treatment. JN. W.

Conversion of Allyl Compounds into Propenyl Compounds.

By A. ANGELI (*Gazzetta*, **23**, ii, 101—102).—On heating safrole at
200° with dry sodium ethoxide (5 per cent.), it is almost wholly con-
verted into isosafrole; this process has the great advantage of
dispensing with the long heating with alcoholic potash which has
hitherto been necessary for the conversion of aromatic allyl deriva-
tives into the corresponding propenyl compounds. It is, in all prob-
ability, applicable to other similar cases. W. J. P.

Action of Nitrous acid on Unsaturated Compounds.

By A.
ANGELI (*Gazzetta*, **23**, ii, 124—135; compare Abstr., 1892, 447,
1198).—A *mononitrosite* of the composition $C_6H_8O_2 \cdot N_2O_3$ is obtained
on passing nitrogen trioxide through an ethereal solution of sorbic
acid; it crystallises in small, white needles melting at about 110°
with decomposition. Neither crotonic acid nor diallyl react with
nitrous acid; stilbene, however, yields a white, crystalline substance
melting at about 132° with decomposition, but no satisfactory analyses
could be made.

On treating safrole with nitrous acid in ethereal or light petroleum
solution, it yields the *α-nitrosite* having the probable constitution
$$CH_2O_2{:}C_6H_3 \cdot CH_2 \cdot \underset{\underset{O-O}{|}}{\overset{\overset{}{|}}{CH}} \cdot \underset{\underset{}{|}}{\overset{\overset{}{|}}{CH_2}}$$
$N \cdot O \cdot N$; it is a yellow powder which melts at about
130° with decomposition, and is sparingly soluble in most solvents.
With piperidine, it does not give a nitrolamine, but a condensation
product which forms small needles melting at 83°, and has the com-
position $C_{15}H_{20}N_2O_4$. On warming with phenylhydrazine, it yields a
compound of the composition $C_{16}H_{17}N_3O_4$, which separates from
benzene in small, yellow needles melting at 87°.
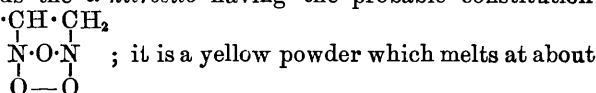
On boiling with alcoholic potash, the α-compound is converted
into the isomeric *β-nitrosite;* this melts at 92°, and is soluble in
alkalis. The author assigns to it the constitution

$$CH_2O_2{:}C_6H_3 \cdot CH_2 \cdot CH(NO_2) \cdot CH{:}NOH,$$

When warmed with concentrated hydrochloric acid, gas is evolved,
and an *aldehyde*, $CH_2O_2{:}C_6H_3 \cdot CH_2 \cdot CH(NO_2) \cdot COH$, is deposited; it
crystallises in lustrous, white scales melting at 86°, and dissolves in
alkalis without decomposition. Its alkaline solution readily reduces
ammoniacal silver nitrate; with phenylhydrazine, it yields a *hydr-
azone* (?), $C_{16}H_{15}N_3O_4$, which melts at 86°. W. J. P.

β-Phenylpropylamine.

By M. FREUND and E. KÓNIG (*Ber.*, **26**,
2874—2875).—β-Phenylpropylamine is obtained by the reducing action

of sodium on methylbenzylic cyanide dissolved in absolute alcohol. The product is distilled with steam, dissolved in hydrochloric acid, and the solution concentrated, and extracted with ether. It is a colourless, highly refractive oil, boils at 210° (uncorr.), has a strong, basic, fishy odour, a strongly alkaline reaction, and absorbs carbonic anhydride from the air. The *hydrochloride* is extremely hygroscopic. The *platinochloride*, $(C_9H_{13}N)_2,H_2PtCl_6$, crystallises in beautiful, lustrous, golden plates, and decomposes at about 140°. The *aurochloride* crystallises from dilute alcohol, and melts at 124°. The *picrate* melts at 182°.   E. C. R.

Oxidation of Azimidotoluene. By J. A. BLADIN (*Ber.*, **26**, 2736—2738; see also Abstr., 1893, i, 375).—A small quantity of azimidobenzoic acid is obtained, together with triazoledicarboxylic acid, by the oxidation of azimidotoluene with alkaline permanganate. The two compounds are easily separated by slightly acidifying the aqueous filtrate with nitric acid and concentrating the solution on the waterbath, when the azimidobenzoic acid is precipitated.

Azimidobenzoic acid, $COOH \cdot C_6H_3 <^{-N}_{NH} \gg N$, crystallises from acetic acid in small, colourless leaflets containing 1 mol. of acetic acid; it does not melt at 270°. The *calcium salt*, $(C_7H_4N_3O_2)_2Ca,4H_2O$, and the *barium salt*, $(C_7H_4N_3O_2)_2Ba,7H_2O$, are described.

Triazoledicarboxylic acid crystallises from water in large, monosymmetric crystals with $2H_2O$. When heated with resorcinol and zinc chloride, it yields a fluorescein which dissolves in ammonia with an intense green fluorescence. The *barium salt*, $C_2N_3H(COO)_2Ba,H_2O$, is an insoluble, crystalline powder. The *copper salt* is bright blue, decomposes on heating, and is soluble in ammonia and mineral acids.

Triazole, $C_2N_3H_3$, obtained by heating the dicarboxylic acid in a current of carbonic anhydride, is a hygroscopic oil, and boils at 208—209° under 742 mm. pressure. The *benzoyl derivative*, $C_2N_3H_2Bz$, crystallises in long, colourless prisms, and melts at 111—115°.
                                                                E. C. R.

Derivatives of Thiosemicarbazide. By G. PULVERMACHER (*Ber.*, **26**, 2812—2813).—By the action in the cold of alkylthiocarbimides on hydrazine hydrate in alcoholic solution, thiosemicarbazides, $NH_2 \cdot NH \cdot CS \cdot NHR'$, are formed. *Phenylthiosemicarbazide*, $NH_2 \cdot NH \cdot CS \cdot NHPh$, prepared from phenylthiocarbimide, forms sixsided prisms, and melts at 140°.   A. R. L.

Action of Acids and Acid Anhydrides on Thiocarbimides. By P. KAY (*Ber.*, **26**, 2848—2852).—Krafft and Karstens (Abstr., 1892, 712) have shown that the di-acid anilides are not produced by the action of acids on the thiocarbimides, but that the mon-acid compounds are formed. The author has, however, succeeded in preparing the di-acid compounds by substituting the acid anhydrides for the acids. *Diacetylallylamine,* $CH_2:CH \cdot CH_2 \cdot N(COMe)_2$, is prepared by boiling allylic thiocarbimide with acetic anhydride, carbon oxy-

sulphide being evolved; it is a colourless liquid, boiling at 88—90° under a pressure of 14 mm. *Diacetanilide*, NPh(COMe)₂, is obtained in a similar manner from phenylthiocarbimide. It forms crystals which melt at 37—37·5°, and is soluble in benzene, but only slightly so in cold water; it boils at 145—146° (13 mm.). *Dipropionanilide*, NPh(COEt)₂, boils at 165—166° (17 mm.), and solidifies in colourless crystals melting at 44°. *Paratolylthiocarbimide* is prepared by boiling paratolylthiocarbanilide with acetic anhydride for 3—4 minutes; it melts at 25° and boils at 245—246°. *Diacetoparatoluidide*, C₆H₄Me·N(COMe)₂, is produced by the further action of acetic anhydride at 170—180°, and boils at 160—161° (15 mm.). *Dibenzanilide*, NPh(COPh)₂, is prepared from phenylthiocarbimide and benzoic anhydride. It melts at 160—161° as stated by Steiner (*Annalen*, **178**, 235).

The following substances have also been prepared by this reaction, the acids and not their anhydrides being employed :—*Allylbenzamide*, COPh·NH·C₃H₅, is a colourless oil with a faint odour and bitter taste. It boils at 173—174° (14 mm.), and decomposes when heated at the ordinary pressure. It combines with bromine to form a *dibromide*, C₁₀H₁₁Br₂NO, which crystallises in lustrous plates, and melts at 135°. When treated with concentrated sulphuric acid, allylbenzamide undergoes intramolecular change, and is converted into the β-methyl-μ-phenyloxazoline which has been previously described by Gabriel and Heymann (Abstr., 1890, 1267) ; it can be very readily prepared by this means, and is also formed when a benzene solution of allylbenzamide is saturated with hydrogen chloride and heated in a sealed tube. A small amount of β-chloropropylbenzamide is also formed by this method. *Allylcinnamide*, CHPh:CH·CO·NH·CH₂·CH:CH₂, forms crystals which melt at 90—90·5°, and boils at 223—224° (14 mm.)'; it combines with 4 atoms of bromine and also with hydrogen chloride. Allylphthalimide, C₈H₄O₂:N·C₃H₅, is prepared from phthalic acid and thiocarbimide; it boils at 295° and melts at 70—71° as stated by Wallach and Kamenski (*Ber.*, **14**, 171). *Allylsuccinimide*, C₄H₄O₂·N·C₃H₅, boils at 130—131° (14 mm.). A. H.

Preparation of Di-acid Anilides. By P. KAY (*Ber.*, **26**, 2853—2856; compare preceding abstract). The di-acid anilides are not formed when the mon-acid derivatives are simply boiled with an acid chloride, but they may be prepared by this reaction if the mixture be heated in an oil bath to a temperature of from 170° to 200° in a flask connected with a reversed condenser. In this way, the acid chloride collects in the tube of the condenser and the anilide is acted on mainly by the superheated vapour. The reaction succeeds better when the acid chloride is gradually added as the conversion proceeds. All the di-acid anilides described in the foregoing abstract have been also prepared in this way. *Diacetorthotoluidide* is a colourless oil which boils at 145° (11 mm.), and does not solidify at the ordinary (summer) temperature. A. H.

The Solid State of some Aldoximes. By E. BOURGEOIS and J. DAMBMANN (*Ber.*, **26**, 2856—2861).—The fact that many of the

aldoximes exist in a solid form has been observed by many chemists. α-Benzaldoxime may be obtained in a pure state by melting the almost pure material, at about 30°, maintaining it at a temperature of 26—27°, and introducing a crystal of the solid compound. Splendid lustrous prisms are formed, which melt sharply at 35°, and may be preserved without change. It boils at 117·5° (14 mm.). When the β-modification, melting at 125°, is slowly heated under diminished pressure, a small amount of it sublimes, but the remainder is converted into the α-form, which suddenly boils up and distils at 117·5° (14 mm.).

Isovaleraldoxime cannot be got to solidify completely. The solid substance melts at 48·5°, and the liquid thus formed boils at 164—165° (corr.), but does not solidify entirely when cooled; the solid matter obtained liquefies in the course of two or three days. The melting point determination is only approximate, the temperature found varying with the length of time for which the sample has been heated; this behaviour of the substance is probably due to the presence of small amounts of impurities. Solid œnanthaldoxime can be prepared much more easily in the pure state, but behaves in a similar manner to the others. It boils at 100·5° under a pressure of 14 mm., but the distillate does not completely solidify. The solid portion melts at 55·5°, and can be preserved without change.   A. H.

Galloparatoluidide. By P. CAZENEUVE (*Compt. rend.*, **117**, 633—635).—When equal weights of crystallised paratoluidine and gallotannic acid are heated together at about 150° for an hour, and the product is treated with dilute hydrochloric acid, and crystallised from dilute alcohol, *galloparatoluidide*, $C_6H_2(OH)_3\cdot CO\cdot NH\cdot C_6H_4Me$, is obtained in white, crystalline plates melting at 211°, only slightly soluble in cold water, but very soluble in hot water, and soluble in alcohol and ether; the crystals contain $2H_2O$, which they lose at 100°. Galloparatoluidide is not affected by alkalis out of contact with air, even in boiling solutions, but in presence of air it is slowly oxidised. When heated with hydrochloric acid in sealed tubes at 150°, it splits up into gallic acid and paratoluidine. Galloparatoluidide yields saline derivatives analogous to those of gallanilide (Abstr , 1893, i, 638). When a boiling solution is mixed with zinc acetate, it yields a very insoluble, white precipitate of the compound

$$OH\cdot C_6H_2(O_2Zn)\cdot CO\cdot NH\cdot C_6H_4Me.$$
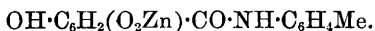
Lead acetate produces a precipitate of similar constitution, and lime water and baryta water yield analogous compounds which alter when exposed to air. Mercuric and cupric acetates are reduced as with gallanilide. When boiled with nitrosodimethylaniline in presence of alcohol, gallotoluidide yields the homologue of gallic blue (Abstr., 1893, i, 510).

Orthotoluidine, methylaniline, dimethylaniline, and the so-called pure xylidine of commerce yield no analogous compounds when heated with gallotannic acid.   C. H. B.

Amido-amidine Bases. By E. LELLMANN and R. HAILER (*Ber.*, **26**, 2759—2763).—The authors have endeavoured to determine to what extent the power of directly dyeing cotton, which is possessed by the monazo-dyes derived from dehydrothioparatoluidine, is dependent on the nature of the elements in the complex $C\ll^{S\cdot C}_{N\cdot C}$, and how far it is conditioned by their arrangement. *Paranitrobenzoparatoluidide*, $NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4Me$, prepared by heating paranitrobenzoic acid with paratoluidine for 5—6 hours at 180—220°, crystallises from glacial acetic acid in greyish-yellow, silky, lustrous needles melting at 203°. *Paranitrobenzometanitroparatoluidide*,

$$NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_3Me\cdot NO_2,$$

is formed from the preceding compound by the action of nitric acid (sp. gr. 1·45) at 0°, and crystallises from alcohol in golden-yellow plates melting at 171—172°; on reducing it with stannous chloride, *paramidobenzenyltoluyleneamidine*, $NH_2\cdot C_6H_4\cdot C\ll^{NH}_{N}>C_6H_3Me$, is obtained, which crystallises from dilute ammonia in small, yellow needles, and melts at 113—114°. The *sulphate*, $C_{14}H_{13}N_3, H_2SO_4 + H_2O$, is crystalline. The diazo-derivative readily dyes cotton.

Metamidobenzenyltoluyleneamidine melts at 238°, instead of at 227—229° as stated by Schack; the sulphate, $(C_{14}H_{13}N_3)_2, H_2SO_4 + 1\frac{1}{2}H_2O$, not $C_{14}H_{13}N_3, H_2SO_4$, crystallises in plates. The tinctorial power of the diazo-derivative is less marked than that of its isomeride. *Paranitrobenzometaxylidide*, $NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_3Me_2$, is prepared by heating paranitrobenzoic acid and metaxylidine at 230°, and crystallises from alcohol in grey prisms melting at 166°. *Paranitrobenzonitrometaxylidide*, $NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_2Me_2\cdot NO_2$, is obtained from the preceding compound in a similar manner to the toluidide; it crystallises from glacial acetic acid, and melts at 139—140°. *Paramidobenzenylmetaxylyleneamidine*, $NH_2\cdot C_6H_4\cdot C\ll^{NH}_{N}>C_6H_2Me_2$, is formed by the reduction of the nitro-compound, and crystallises from dilute ammonia in slender, almost colourless needles melting at 183°. The *sulphate*, $C_{15}H_{15}N_3, H_2SO_4 + 6H_2O$, is deposited in slender, colourless, lustrous needles. The tinctorial power of the diazo-derivative was not determined. J. B. T.

Protocatechuic Aldehyde and Piperonal. By R. WEGSCHEIDER (*Monatsh.*, **14**, 382—389).—In order to convert piperonal into protocatechuic aldehyde, it is not necessary to isolate the dichloropiperonal (compare Fittig and Remsen, *Annalen*, **159**, 148). Piperonal (28 grams) is shaken with phosphorus pentachloride (120 grams) in a reflux apparatus, the temperature not being allowed to rise, and the action is completed by heating the mixture at 108—109°; the product is then treated with water (1512 c.c.), and the mixture heated, and finally boiled. The lower oily layer, which contains the protocatechuic aldehyde, is extracted with ether, and the aldehyde

thus obtained is recrystallised from toluene; the yield is 80 per cent. Opianic acid yields only 8 per cent. of protocatechuic aldehyde when boiled with hydrochloric acid, and the intermediate product, vanillin, yields 20 per cent.

Protocatechuic aldehyde melts at 153—154°. The *lead* and *mercury* compounds and the *oxime* are described. The *phenylhydrazone* exists in two, probably stereoisomeric, modifications. The first, which melts at 174—175°, is formed when cold alcoholic solutions of the aldehyde and phenylhydrazine are mixed. The second is obtained on heating the first with an alcoholic solution of phenylhydrazine, and melts at 127—128°; in contact with cold water, it is slowly transformed into the first modification.

An attempt to synthesise piperonal from protocatechuic aldehyde and trioxymethylene yielded only traces, whilst by heating the lead and mercury compounds with methylenic iodide, none was formed; when, however, the aldehyde (5 grams) was heated with methylenic iodide (14.7 grams) and alcoholic potash (6.3 grams in 10 c.c. of methylic alcohol) for $9\frac{1}{2}$ hours at 100°, and then for $2\frac{3}{4}$ hours at 135—140°, a small amount (0.020 gram) of piperonal was obtained (m. p. 35—36°); the piperonic acid, obtained on oxidising it with permanganate, melted at 221.5—224.5°.   Jn. W.

Violet Perfume. By F. TIEMANN and P. KRÜGER (*Ber.*, **26**, 2675—2708).—The characteristic fragrance of violets is also possessed by dried iris root, which has been employed by the authors as the source of the fragrant oil which forms the subject of the present paper. It has been found impossible to obtain sufficient material from violet blossoms themselves to ascertain whether the odoriferous substance contained in them is or is not identical with those described.

To isolate the fragrant oil, the dried iris root is repeatedly extracted with ether, and the extracted matter then distilled with steam. The non-volatile portion consists mainly of resinous matter and a little myristic acid, irigenin, iridic acid, &c., whilst the readily-volatile fraction contains the *irone* or fragrant oil, together with a considerable amount of myristic acid and its methylic salt, oleïc acid, an ethereal oleate, oleïc aldehyde, and small amounts of other substances. The acids and ethereal salts are removed from the more volatile portion, obtained by the repeated fractional distillation of the oil with steam, by dissolving it in cold alcoholic potash and precipitating with water. Aldehydes are next oxidised by warming with water and silver oxide, and the irone finally purified by conversion into the phenylhydrazone, which is then decomposed by distillation with dilute sulphuric acid.

Irone, $C_{13}H_{20}O$, is an oil which is scarcely soluble in water, readily in alcohol, &c., boils at 144° under a pressure of 16 mm., and has a sp. gr. of 0.939 at 20°. Its index of refraction, n_D, is 1.50113, and it is dextrorotatory. The smell of the pure substance is sharp, and, in the concentrated form, quite unlike that of violets, but when largely diluted resembles that of the natural flowers. The *phenylhydrazone* is a yellowish-brown oil. The *oxime*, $C_{13}H_{20}$:NOH, crystallises with

very great difficulty in lustrous, white plates melting at 121·5°, but is generally obtained as an oil. Irone is a methyl ketone, yielding chloroform on treatment with sodium hypochlorite.

When treated with hydriodic acid and phosphorus, irone loses a molecule of water, and forms *irene*, $C_{13}H_{18}$, which is a colourless oil boiling at 113—115° (9 mm.). It has a sp. gr. of 0·9402 at 20°, and a refractive index of 1·5274. It dissolves in concentrated sulphuric acid at the ordinary temperature, decolorises a solution of bromine in acetic acid, and is gradually converted into a resin by the action of the air. When oxidised with vigorous reagents, irene is broken up into compounds containing only a small number of carbon atoms, such as formic, acetic, and pyruvic acids; but when the oxidation is more carefully conducted, a series of compounds is obtained the nature of which throws much light on the constitution of irene itself and irone.

Oxydihydroxydehydroirene, $C_6H_3Me\!<\!^{CMe_2 \cdot CH \cdot OH}_{CO—CH \cdot OH}$, formed by the action of chromic acid in acetic acid solution, crystallises in highly refractive rhombohedra melting at 154—155°, and has feebly acid properties.

Iregenonedicarboxylic acid, $COOH \cdot CO \cdot C_6H_3Me \cdot CMe_2 \cdot COOH$, is produced by the action of alkaline permanganate on the foregoing compound. It crystallises from hot water in short needles or oblique prisms melting at 227°.

Iregenonetricarboxylic acid, $COOH \cdot CO \cdot C_6H_3(COOH) \cdot CMe_2 \cdot COOH$, is formed by the further oxidation of the foregoing, and crystallises from water, at 5°, in granular prisms containing water of crystallisation. At 110°, the crystals become anhydrous, and melt with decomposition at 227°. The *trimethylic salt* forms compact crystals melting at 127—128°.

Ioniregenetricarboxylic acid, $C_6H_3(COOH)_2 \cdot CMe_2 \cdot COOH$, is the final product of the oxidation of irene, when this is carried out at first by gentle, and then by more powerful, oxidisers. It crystallises in white needles, and is slightly soluble in hot water, alcohol, and ether. At 150° it loses water, and is converted into an anhydride which is also formed when iregenonetricarboxylic acid is heated above its melting point, carbonic oxide and water being evolved. The salts of the acid, which are also formed by dissolving the anhydride in alkalis, crystallise well. The acid is very stable, and is not altered by oxidising agents or by warm concentrated sulphuric acid. The anhydride can be distilled without decomposition. The *trimethylic salt* crystallises in colourless needles melting at 93°. The *anhydride*, $COOH \cdot C_9H_9\!<\!^{CO}_{CO}\!>\!O$, crystallises from benzene in plates melting at 214°. When the ammonium salt of ioniregenetricarboxylic acid is heated in a current of carbonic anhydride, the corresponding imido-acid, $COOH \cdot C_9H_9\!<\!^{CO}_{CO}\!>\!NH$, is produced. It is a white, crystalline powder which is insoluble in the usual solvents, melts above 300°, and boils a few degrees higher than this. Its *silver salt* is a white powder, which, when heated in a current of carbonic anhydride,

yields the imide of dimethylhomophthalic acid, $C_6H_4 <^{CMe_2 \cdot CO}_{CO-NH}$, previously prepared by Gabriel (Abstr., 1887, 725).

The oxidation products of irene may therefore be looked on as derived from a hypothetical substance, dehydroirene, of the formula $C_6H_3Me <^{CMe_2 \cdot CH}_{CH_2-CH}$ or $C_6H_3Me <^{CMe_2 \cdot CH_2}_{CH=CH}$.
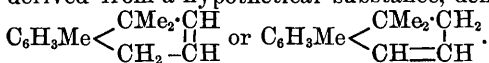
In order to throw further light on the constitution of irone and irene, a series of synthetical researches was made, starting with geranaldehyde (citral), a substance which has been shown by Semmler (Abstr., 1891, 540) to have the constitution $CHMe_2 \cdot CH_2 \cdot CH:CH \cdot CMe:CH \cdot COH$, since, when treated with potassium hydrogen sulphate or hydriodic acid, it is quantitatively converted into cymene.

Geranaldehyde undergoes condensation with acetone, yielding *pseudoionone*, $CHMe_2 \cdot CH_2 \cdot CH:CH \cdot CMe:CH \cdot CH:CH \cdot COMe$. This substance is an oil, boiling at 143—145° (12 mm.), has a sp. gr. of 0·9044, and a refractive index of 1·5275. The *phenylhydrazone* and the *oxime* are thick oils. It does not combine with sodium hydrogen sulphite.

When pseudoionone is heated with dilute sulphuric acid and a little glycerol, it is converted into the isomeric *ionone*, $C_{13}H_{20}O$. This substance boils at 126—128° at 12 mm., has a sp. gr. of 0·9351, and a refractive index of 1·507, and is optically inactive. It has a characteristic odour resembling that of violets, and, at the same time, that of the vine blossom. When heated with hydriodic acid and phosphorus, it loses water, and yields *ionene*, $C_{13}H_{18}$, which boils at 106—107° (10 mm.), has a sp. gr. of 0·9338, and a refractive index of 1·5244. It resembles irene very closely, and, like it, has the properties of a terpene. When cautiously oxidised with chromic acid, it yields a mixture of the following compounds, which can be separated by means of their calcium salts.

Iongenogonic acid, $C_6H_3Me <^{CMe_2}_{CO-} > CH \cdot COOH$, forms white needles melting at 237°.

Ionegenedicarboxylic acid, $COOH \cdot C_6H_3Me \cdot CMe_2 \cdot COOH$, forms vitreous prisms readily soluble in alcohol, &c., but only slightly in boiling water. When rapidly heated, it melts at 130—131°, but when gradually heated at a few degrees lower, it is converted into the *anhydride*, which crystallises from light petroleum in long, white needles melting at 105°. The acid is bibasic, and its calcium salt, when distilled with soda lime, yields cymene. *Ionegenealide*, $C_6H_3Me <^{CMe_2 \cdot CH \cdot OH}_{CO-O}$, crystallises from benzene in transparent plates melting at 175°. This substance possesses feeble acid properties, and has the composition of the semi-aldehyde of *ionegenedicarboxylic acid*. It does not, however, appear to contain the aldehyde group, and is therefore probably an anhydride of the constitution shown. It is very readily converted by oxidation into ionegenedicarboxylic acid.

Ionene is converted, by oxidation with alkaline permanganate, into

ionegenonetricarboxylic acid, $C_6H_3(COOH)_2 \cdot CMe_2 \cdot CO \cdot COOH$, which crystallises with $2H_2O$. When rapidly heated, it melts at 140—145°, and decomposes above this temperature, the anhydride of ioniregene-tricarboxylic acid being formed. The final product of the oxidation of ionene itself, and of the oxidation products just described, is ioni-regenetricarboxylic acid, identical with that obtained from irene.

The isomeric hydrocarbons, irene and ionene, are shown by the nature of their oxidation products to be trimethyl derivatives of a tetrahydronaphthalene. They both contain three ethylene linkings (refractive index), of which two are probably in the ring which by the removal of two hydrogen atoms is converted into the benzene ring, as this is necessary to account for the terpene-like properties of the two substances. The constitution of ionene follows from that of ionone, which is shown, by its formation from pseudoionone by intra-molecular change, to be probably

$$CH_2 \cdot CMe_2 \cdot CH \cdot CH \colon CH \cdot COMe$$
$$CH \colon CH \text{---} CHMe$$
I. Ionone.
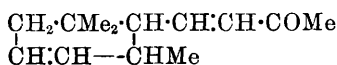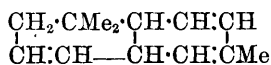
$$CH_2 \cdot CMe_2 \cdot CH \cdot CH \colon CH$$
$$CH \colon CH \text{---} CH \cdot CH \colon CMe$$
II. Ionene.

Ionene therefore has the formula II, whilst the constitution of the isomeric irene is most probably represented by IV. Irone is related to irene in the same way as ionone to ionene, and therefore has the formula III,

$$CH \cdot CMe_2 \cdot CH \cdot CH \colon CH \cdot COMe$$
$$CH \cdot CH_2 - CHMe$$
III. Irone.
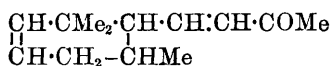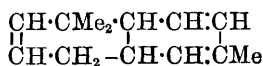
$$CH \cdot CMe_2 \cdot CH \cdot CH \colon CH$$
$$CH \cdot CH_2 - CH \cdot CH \colon CMe$$
IV. Irene.

Ionone and irone are both without injurious effect on the animal organism. The odours of ionone and irone are extraordinarily alike, and can only be distinguished by observers of great experience, and this is looked on by the authors as an additional confirmation of the great similarity in constitution of the two compounds.

It is probable that either irone, ionone, or some optically isomeric substance is present in the blossoms of the violet, but this question has not yet been decided experimentally. A. H.

Compounds of the Geranaldehyde (Citral) Series. By F. Tiemann and F. W. Semmler (*Ber.*, 26, 2708—2729).—Geranaldehyde (citral), $CHMe_2 \cdot CH_2 \cdot CH \colon CH \cdot CMe \colon CH \cdot COH$ (Abstr., 1891, 539), is converted, by careful reduction with sodium and alcohol, into optically inactive geraniol, $CHMe_2 \cdot CH_2 \cdot CH \colon CH \cdot CMe \colon CH \cdot CH_2 \cdot OH$, and can be obtained from the latter by oxidation (Abstr., 1891, 30). Several substances of the formula $C_{10}H_{18}O$ isomeric with geraniol are known. Among these are coriandrol, which is dextrorotatory (Abstr., 1891, 540); rhodinol, feebly lævorotatory (Abstr., 1892, 203); and linaloöl. The rotation of the last of these compounds varies with the origin of the substance, but it is probable that the compounds described as aurantiol, lavendol, nerolol, and linaloöl (Abstr., 1892, 868, 1236) are in reality identical, the slight differences observed between them

being due to accidental impurities. All these compounds of the formula $C_{10}H_{18}O$, as well as geraniol, are converted by cautious oxidation into geranaldehyde. In order to account for the existence of these optically active forms isomeric with geraniol, it is necessary to assume that they have a different structural formula from the latter, such as $CMe_2:CH·CH:CH·CHMe·CH_2·CH_2·OH$ or

$$CH_2:CMe·CH_2·CH:CH·CHMe·CH_2·CH_2·OH,$$

and that on oxidation a change in the position of the ethyleen linking, analogous to that observed by Fittig, takes place.

Geranaldoxime, $C_{10}H_6:NOH$, is a yellow oil, boiling at 143—145° (12 mm.), and has a sp. gr. of 0·9386 at 20° and a refractive index $[n]_D$ of 1·51433. When distilled at the ordinary pressure, the corresponding nitrile is formed. *Geranalphenylhydrazone*, $C_{10}H_6:N_2HPh$, is a red oil which cannot be distilled. *Geranalanilide*, $C_{10}H_{16}:NPh$, is obtained by heating the constituents together at 150°. It is a yellow oil boiling at 200° (20 mm.).

Geranionitrile, $C_9H_{15}·CN$, is prepared by heating geranaldoxime with acetic anhydride. It is a colourless liquid which boils at 110° (10 mm.), has a sp. gr. of 0·8709 at 20°, and a refractive index of 1·4759. When digested with an alcoholic solution of hydroxylamine, an oily amidoxime is formed.

Geranic acid, $C_9H_{15}·COOH$, can be obtained from the nitrile by the action of alcoholic potash much more readily than by the oxidation of geranaldehyde with silver oxide (Abstr., 1891, 323). It is an oil, boils at 153° (13 mm.), has a sp. gr. of 0·964 at 20°, and a refractive index of 1·4797. Its odour resembles that of the higher fatty acids.

When geranaldehyde is carefully oxidised with chromic acid at a low temperature, an uncrystallisable acid of the formula

$$CHMe_2·CH_2·CH:CH·CMe(OH)·CH(OH)·COOH$$

is obtained, together with methyl hexylene ketone. The same products are obtained, under the same conditions, from geraniol.

Methylhexylenecarbinol, $CHMe_2·CH_2·CH:CH·CHMe·OH$, is formed, together with geranic acid and methyl hexylene ketone, in the hydrolysis of geranionitrile. It boils at 175°, has a sp. gr. of 0·8545 at 20°, and an index of refraction of 1·4505. This substance is identical with the compound previously prepared by Wallach by the reduction of methyl hexylene ketone (Abstr., 1893, i, 598).

Methyl hexylene ketone, $CHMe_2·CH_2·CH:CH·COMe$, has been previously described by Wallach (Abstr., 1890, 1314). The formula ascribed above to this compound differs from that proposed by Wallach, $CHMe_2·CH:CH·CH_2·COMe$. The authors point out that their formula explains the various reactions of the compound, and is, moreover, in agreement with the formulæ of the other compounds derived from geranaldehyde; they propose to examine the question further.

Methyl hexylene ketone is converted by the action of bromine and soda into *tribromomethylhexylcarbinol*, $C_8H_{12}Br_3O·OH$, which separates from light petroleum in snow-white crystals melting at 98—99°.

Geraniolene, $CHMe_2 \cdot CH_2 \cdot CH:CH \cdot CMe:CH_2$, is formed when geranic acid is distilled at the ordinary pressure, carbonic anhydride being evolved. It boils at 142—143°, has a sp. gr. of 0·757 at 20°, and a refractive index of 1·4368. It combines with 4 atoms of bromine, forming an oily additive compound, $C_9H_{16}Br_4$.

Geranic acid, its nitrile, and geraniolene are, like pseudoinone (see preceding abstract), converted into cyclic compounds of the same molecular weight by the action of dilute acids.

Isogeranic acid, $CH\!\!<^{CH_2 \cdot CMe_2}_{CH \cdot CHMe}\!\!>CH \cdot COOH$, is obtained by shaking the oily geranic acid with 65 per cent. sulphuric acid. It crystallises from water or light petroleum in white needles melting at 103·5°, and is only slightly soluble in hot water, readily in alcohol and ether. It boils at 138° (11 mm.), and can also be distilled without decomposition at the ordinary pressure. The *dibromide* is formed by the direct addition of bromine, using a solution in chloroform. It separates from light petroleum in white crystals melting at 121°.

Dihydroxydihydroisogeranic acid,

$$OH \cdot CH\!\!<^{CH_2\underline{\qquad}CMe_2}_{CH(OH) \cdot CHMe}\!\!>CH \cdot COOH,$$
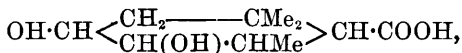
is formed by the action of potassium permanganate on a solution of the acid in sodium carbonate. It separates from absolute alcohol in well-developed crystals melting at 195—196°.

Isogeranionitrile, $CH\!\!<^{CH_2 \cdot CMe_2}_{CH \cdot CHMe}\!\!>CH \cdot CN$, is formed from the nitrile of geranic acid by the action of 70 per cent. sulphuric acid. It boils at 87—88° (11 mm.), has a sp. gr. of 0·9208 at 20°, and an index of refraction of 1·4734. When the nitrile is hydrolysed, isogeranic acid is obtained. The *amidoxime* of the nitrile is solid, and melts at 165°.

Isogeraniolene, $CH\!\!<^{CH_2 \cdot CMe_2}_{CH \cdot CHMe}\!\!>CH_2$, is produced in a similar manner from geraniolene; it boils at 138—140°, has a sp. gr. of 0·7978 at 22°, and an index of refraction of 1·4434.

It will be observed that all the cyclic isomerides have a lower boiling point, higher sp. gr., and somewhat lower index of refraction than the corresponding members of the geranaldehyde series.

A. H.

Synthesis of Aromatic Hydroxyketones. By M. NENCKI (*J. Russ. Chem. Soc.*, **25**, 110—124).—Zinc chloride (15 grams) is dissolved in glacial acetic acid (40 grams), and to the solution dry gallobenzophenone (10 grams) is added, the mixture being heated on the water bath in a flask connected with a reflux condenser until the ketone is completely dissolved. Phosphorus oxychloride is then added drop by drop, and after 10 minutes' heating the mixture is poured into cold water. Recrystallisation from boiling alcohol gives rhombic needles which melt at 165°. The substance is a double ketone, $COPh \cdot C_6H(OH)_2(OAc) \cdot COMe$, whose monophenylhydrazone melts at 248—249°.

Hydrolysis of the compound $C_{17}H_{14}O_6$, by means of 70 per cent.

sulphuric acid, yielded the compound $COPh \cdot C_6H(OH)_3 \cdot COMe$; this
gives a diphenylhydrazone melting at 233—234°.

Chloracetic acid and phenol, with phosphorus oxychloride, or
zinc chloride, give the ethereal salt $CH_2Cl \cdot COOPh$ (m. p. 44°).
Pyrogallol behaves differently from phenol, giving, with phosphorus
oxychloride and chloracetic acid, the ketone $C_6H_2(OH)_2 \cdot CO \cdot CH_2Cl$.
This gallochloracetophenone melts at 167—168°, is easily soluble in
alcohol, ether, and boiling water, but only sparingly in cold water.
Phenylhydrazine gives a hydrazone-hydrazide, $C_{20}H_{20}O_3N_4$, which
melts at 197—198°. Aniline gives the compound

$$C_6H_2(OH)_3 \cdot CO \cdot CH_2 \cdot NHPh,$$

which melts at 132°, and may be recrystallised from alcohol or
boiling benzene. Caustic alkalis or calcium carbonate give the
oxide $C_6H_2(OH)_2 {<}^{-O-}_{CO}{>} CH_2$ soluble in boiling water, and melting at
224°.

Gallobromacetophenone may be obtained by using bromacetic
instead of chloracetic acid. It melts at 159°.   J. W.

Dimethylamidobenzoic acids. By C. LAUTH (*Compt. rend.*, **117**,
581—583).—*Orthodimethylamidobenzoic acid* is obtained by the action
of methylic iodide on a hot alcoholic solution of sodium orthamido-
benzoate. It crystallises in long needles melting at 175°, dissolves in
500 parts of cold water, and is very soluble in alcohol, ether, and
benzene, forming solutions which have a blue fluorescence. It combines
with both acids and alkalis, forms no nitroso-compound, but yields
yellow, orange, or brown colouring matters with diazo-derivatives.
When treated with oxidising agents, and especially with cupric
chloride or chloranil, it yields a reddish-violet colouring matter,
$COOH \cdot C_6H_3(NH_2) \cdot C(OH)[C_6H_3(NMe_2) \cdot COOH]_2$, which has the
general properties of triphenylmethane derivatives, together with
special properties resulting from the presence of the COOH group;
it is soluble in alkalis, and is precipitated from its solutions by acids,
dyes metallic mordants, and also dyes wool and cotton mordanted
with tannin, in the same way as basic colouring matters.

Orthodimethylamidobenzoic acid condenses with tetramethyl-
diamidobenzhydrol, and, after oxidation with lead peroxide, yields a
blue-violet monocarboxyhexamethylrosaniline. With benzaldehyde
or metanitrobenzaldehyde, it yields a beautiful blue colouring matter,
$OH \cdot CPh[C_6H_3(NMe_2) \cdot COOH]_2$, which dissolves in alkalis, and dyes
wool and mordanted cotton.

Paradimethylamidobenzoic acid is obtained in a similar manner. It
yields no colouring matter when oxidised, and with condensing
reagents, it yields hexamethylrosaniline-violet and malachite-green,
which do not contain the carboxyl group.

Metadimethylamidobenzoic acid, prepared in a similar way, or by
transforming Griess' benzobetaïne, yields no colouring matters, either
with oxidising or with condensing reagents.

It would seem that the introduction of the group COOH into

dimethylaniline, and the orientation of this group with respect to the NH_2 group, confers peculiar properties on each of the three isomerides, and determines whether, on oxidation or condensation, they will yield colouring matters containing the carboxy-group, colouring matters not containing this group, or no colouring matters at all.

<div align="right">C. H. B.</div>

Ethereal Salts of Anhydrohippuric acid. By F. WEISS (*Ber.*, **26**, 2641—2645).—The phenylic anhydrohippurate obtained by the action of phosphorus oxychloride on phenylic hippurate is found by the cryoscopic method to have the formula assigned to it (Abstr., 1893, i, 579); the constitutional formula which best explains its behaviour is $NBz{<}{\overset{CH}{\underset{COPh}{\|}}}$. It combines with 2 atoms of chlorine forming a compound which readily loses hydrogen chloride. If treated with phosphorus pentachloride, the product, on hydrolysis with water, yields *phenylic hydroxyhippurate*, $NHBz{\cdot}CH(OH){\cdot}COOPh$, which melts at 170°, and when heated with alkalis decomposes into benzamide, phenol, and glyoxylic acid. The homologous *compound* $NHBz{\cdot}CMe(OH){\cdot}COOPh$ (from phenylic anhydro-α-benzoylamidopropionate) melts at 134°. If the hydroxyl group in these compounds were replaced by the group SPh, derivatives of the mercapturic acids would be obtained.

<div align="right">A. R. L.</div>

Hexahydrosalicylic acid. By A. EINHORN and R. WILLSTÄTTER (*Ber.*, **26**, 2913—2914).—By the action of sodium on salicylic acid in amylic alcoholic solution *hexahydrosalicylic acid*,

$$OH{\cdot}C_6H_{10}{\cdot}COOH,$$
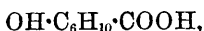
is formed, together with a mixture of various other acids which have not been investigated. It is readily soluble in water, and crystallises in prismatic needles, or tetragonal plates, melting at 105°. The acid gives no coloration with ferric chloride, and, in alkaline solution, decolorises potassium permanganate slowly; it boils without decomposition under the ordinary pressure, and the odour of the vapour resembles that of the higher fatty acids; the crystals are odourless. Anthranilic acid, on reduction in a similar manner, yields hexahydrosalicylic acid and ammonia. The *methylic salt* is a colourless liquid, with an ethereal fruity smell; it boils without decomposition, and gives no coloration with ferric chloride.

Metahydroxybenzoic acid yields two acid reduction products; both crystallise readily, and melt at 112—114° and 130° respectively. Paramidobenzoic acid and dimethylparamidobenzoic acid are converted on reduction into a crystalline acid which melts at about 40°. β-Naphtholcarboxylic acid yields an acid melting at 141°. Thymotic acid has also been reduced in the same manner.

By the action of sodium on tetrahydroparatoluic acid dissolved in ethylic alcohol, *hexahydroparatoluic acid* is formed; it is liquid at ordinary temperatures, and boils at 245—248°. The *amide* melts at 195°. α-*Bromohexahydroparatoluic acid* melts at 94°, and on treatment with quinoline, yields tetrahydroparatoluic acid (m. p. 47°).

The authors points out that v. Baeyer (1879) was the first to employ sodium as a reducing agent in ethylic, or amylic alcoholic solution, and therefore that the method should bear his name rather than Wischnegradsky's, Ladenburg's, or Bamberger's.

<div align="right">J. B. T.</div>

Canaigre Tannin. By H. TRIMBLE and J. C. PEACOCK (*Pharm. J. Trans.*, **53**, 42—45).—Canaigre is the tuberous root of *Rumex hymenosepalus*, growing abundantly in the sandy soil of Texas, New Mexico, and Arizona. The green roots contain 11·46 per cent. tannin (by hide) of 71 per cent. purity. The paper describes in detail the extraction of the tannin, its chemical characteristics, and behaviour with various reagents. The results indicate that this tannin belongs to the group of which those from mangrove and rhatany are typical examples.

<div align="right">R. R.</div>

Hydroxy-β-phenylcoumarin. By S. v. KOSTANECKI and C. WEBER (*Ber.*, **26**, 2906—2908).—Metadihydroxy-β-phenylcoumarin is not obtained when phroglucinol and ethylic benzoylacetate are treated with concentrated sulphuric acid. Ethylic benzoylacetate, however, easily condenses with pyrogallol in the presence of sulphuric acid, and yields *β-phenyldaphnetin*, $C_{15}H_{10}O_4$; this crystallises with $1H_2O$ in long, lustrous, yellowish needles, loses its water at 100°, and then melts at 190—192°. It gives a red solution with alkalis, and with ferric chloride a green coloration which turns red on the addition of soda. Ammoniacal silver solution is easily reduced by it with formation of a mirror. The *diacetyl compound* crystallises in broad, white needles, and melts at 133—134°.

Metadihydroxy-β-phenylcoumarin, $C_{15}H_{10}O_4$, is obtained by warming ethylic benzoylacetate with phloroglucinol and zinc chloride on the water bath. It crystallises in colourless needles, melts at 234—235°, is indifferent to mordants, and reduces ammoniacal silver solution. It gives an intense yellow solution with alkalis, and a dirty violet coloration with ferric chloride. It is evidently not identical with chrysin. The *diacetyl compound* crystallises in white, prismatic needles, and melts at 180—181°.

<div align="right">E. C. R.</div>

Conversion of Diphenylsulphone into Diphenylic Sulphide and Diphenylic Selenide. By F. KRAFFT and W. VORSTER (*Ber.*, **26**, 2813—2822).—Diphenylsulphone melts at 128°, and boils at 232·5° (18 mm.). When a mixture of diphenylsulphone and sulphur is heated to its boiling point, sulphurous anhydride, diphenylic sulphide, and diphenylic bisulphide pass over. The bisulphide is formed by the action of sulphur on the monosulphide, and when heated with phenylsulphone, it is converted into the monosulphide. The yield of the bisulphide may, therefore, be reduced to a minimum by the following method :—The mixture (above mentioned) is heated in a retort until sulphurous anhydride ceases to be evolved, the cause of which is that the boiling point of the diphenylic sulphide (292°), which then forms the main portion of the product, is below the temperature at which the reaction takes place. The phenylic

sulphide is now distilled off, and the residue subsequently reheated, when the bisulphide reacts with the sulphone, producing more mono-sulphide. Diphenylic sulphide boils at 157—158° (16·5° mm.), and its sp. gr. at 15·2° is 1·1175.

ββ-Dinaphthylic sulphide is obtained from ββ-dinaphthylsulphone (m. p. 177°) and sulphur. Dipara- and dimeta-tolylsulphone do not react in the same manner as the above-mentioned sulphones.

Phosphorus in either of its forms appears not to interact with diphenylsulphone even at 250°.

When diphenylsulphone is heated with red selenium, the latter is first converted into the grey modification, which subsequently dissolves in the fused sulphone; if the product is distilled, after the evolution of sulphurous anhydride has ceased, *diphenylic selenide*, Ph_2Se, passes over. On reheating the residue and again distilling, a further quantity of diphenylic selenide is obtained. It is a colourless, highly refractive oil, resembling the sulphide, boils at 301—302° under ordinary pressure, and at 167° under a pressure of 16·5° mm. Its sp. gr. at 15·2° is 1·3561. Negative results were obtained with diphenylsulphone and tellurium.

Diphenylic sulphide forms a dibromo-substitution derivative, but when bromine is added to a cold ethereal or alcoholic solution of diphenyl selenide, a *dibromo*-additive compound, Ph_2SeBr_2, separates as an orange-red, crystalline precipitate which melts at 140° with decomposition. When the dibromide is boiled with alcohol or water, or, preferably, gently warmed with 15 per cent. sodium hydroxide, *diphenylic selenoxide*, Ph_2SeO, is formed. It is a white substance which, when dried in a vacuum, melts at 113—114°. If heated in a tube over a direct flame, slight detonation accompanied by a reddish flash occurs, and an oil is formed; when a small quantity is distilled under diminished pressure, diphenylic selenide passes over. Diphenylic selenoxide yields a *dichloride*, Ph_2SeCl_2, when treated with hydrochloric acid; it melts at 179—180°.

Experiments made with the object of preparing a selenone by oxidising diphenylic selenide with potassium dichromate showed that diphenylic selenoxide is obtained under these circumstances.

When diphenylsulphone is dissolved in hot xylene, and sodium is added, benzenesulphinic acid and diphenyl are formed. To isolate the sulphinic acid, the product is shaken with water, the aqueous solution of the sodium salt concentrated in an atmosphere of carbonic anhydride, and hydrochloric acid added in the cold, when the sulphinic acid separates. A. R. L.

Action of Sulphuric Anhydride on Nitriles. By P. EITNER (*Ber.*, **26**, 2833—2839; compare Abstr., 1892, 713).—Sulphuric anhydride combines with acetonitrile to form an additive product of the formula $3MeCN,2SO_3$, which is a very hygroscopic, sandy, yellow mass, readily soluble in water, insoluble in all indifferent solvents. The *hydrate*, $3MeCN,2SO_3 + H_2O$, is precipitated as a white, flocculent mass on adding alcohol and ether to an aqueous solution of the substance. Its solution is strongly acid, but definite salts have not been obtained.

When fuming sulphuric acid is substituted for the sulphuric anhydride, an additive compound of the formula $2MeCN,SO_3$ is obtained as a yellow, crystalline mass, which combines with $1H_2O$. The substance thus formed is analogous to that obtained in a similar manner from benzonitrile, and is therefore probably *acetylsulphacetamidinic acid*, $COMe \cdot NH \cdot CMe \vdots N \cdot SO_3H$. This formula is confirmed by the fact that the aqueous solution of the compound, after a time, contains diacetamide, $NH(COMe)_2$, and amidosulphonic acid, NH_2SO_3H.

Paratoluonitrile is converted by the action of sulphuric anhydride into *paratoluylsulphoparatolenylamidinic anhydride*,

$$SO_2 {\Large<}{}^{N \vdots C(C_6H_4Me)}_{O \cdot C(C_6H_4Me)}{\Large>}N.$$
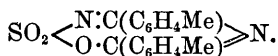
It is a yellow, sandy mass, which is scarcely hygroscopic, and crystallises from benzene in colourless, lustrous prisms, containing $\frac{1}{2}$ mol. benzene; it turns yellow at $145°$, and melts at $161 \cdot 5$—$162°$. When treated with concentrated sulphuric acid, it is decomposed with formation of imidodiparatoluylamide, $C_6H_4Me \cdot CO \cdot NH \cdot C(C_6H_4Me) \vdots NH$, and finally of diparatoluylamide, $NH(CO \cdot C_6H_4Me)_2$. When its solution in benzene is digested with water and alcohol, ethylic paratoluate and *sulphoparatolenylamidinic acid*, $SO_3H \cdot N \vdots C(NH_2) \cdot C_6H_4Me$, are produced. The latter is a white powder, which does not undergo alteration in the air, crystallises from water or alcohol in prisms, and melts at 250—$251°$. The *barium salt* crystallises in splendid, colourless prisms.

When sulphoparatolenylamidinic acid is treated with dilute sulphuric acid, it is decomposed into sulphuric acid and the corresponding *amidine*, $HN \vdots C(NH_2) \cdot C_6H_4Me$, which is obtained in the form of the *acid sulphate*. This salt forms fine, white plates, melts at 240—$241°$, and is readily soluble in water and alcohol, almost insoluble in ether.

Paratoluonitrile therefore behaves towards sulphuric anhydride in a manner precisely similar to benzonitrile. A. H.

2′ : 3′-Diphenylindoles. By F. R. JAPP and T. S. MURRAY (*Ber.*, **26**, 2638—2641).—The authors observed that 2′ : 3′-diphenylindoles are formed by heating to its boiling point a mixture of benzoïn with an excess of a primary aromatic amine in presence of zinc chloride, and in this way they had prepared a number of these compounds, which were, however, in the meantime, described by Bischler and Firemann (Abstr., 1893, i, 519), the latter having obtained them by heating desyl anilide or desyl bromide with an aromatic amine. The authors show that desyl anilide (*loc. cit.*) and Voigt's anilbenzoïn (*J. pr. Chem.*, **31**, 544; **34**, 2) are one and the same substance; it melts at 98—99°.

Indole derivatives are only obtained from desyl anilide and an amine in presence of a trace of desyl bromide; they are formed, however, when desyl bromide is heated with an amine, a fact which indicates that the eliminated hydrogen bromide effects the condensation of the initially formed desyl anilide. The authors then found

that indole derivatives are obtained by heating desyl anilide with a mixture of an amine and its hydrochloride, which led to the discovery that by boiling benzoïn with a mixture of an amine and its hydrochloride, a much better yield of indole derivative is obtained than by the use of zinc chloride (see above). The zinc chloride method is, however, the better one for the preparation of 2' : 3'-di-phenyl-β-naphthindole, because of the tendency to form β-dinaphthyl-amine (Bischler and Fireman, *loc. cit.*).

2' : 3'-Diphenylorthotolindole (*loc. cit.*) melts at 135—136° (not 128°).

2' : 3'-*Diphenyl-α-naphthindole*, $C_{10}H_6{<}^{CPh}_{NH}{>}CPh$, forms colourless needles, and melts at 141°.

The compounds prepared by Lachowicz (this vol., i, 39) by the action of aniline hydrochloride and its analogues on benzoïn at 160° are probably the intermediary substances in the formations of indoles.

A. R. L.

2 : 3-Hydroxynaphthoic acid. By S. v. KOSTANECKI (*Ber.*, **26,** 2897—2900).—*Phenylazohydroxynaphthoic acid* [PhN$_2$: OH : COOH = 1 : 2 : 3] is obtained from the hydroxy-acid in the usual way. It crystallises in reddish-brown needles, melts at 232°, and only yields pale colours with mordants after some time, probably on account of the insolubility of the dye.

Nitrosohydroxynaphthoic acid crystallises in red tablets, melts at 185° with decomposition, gives a brownish-yellow coloration with concentrated sulphuric acid, and a beautiful green with iron mordants, which is, however, unstable to boiling soap solution.

Naphthalenedioximeanhydridecarboxylic acid, $COOH \cdot C_{10}H_5{\ll}^N_N{>}0$,

is obtained by heating the above nitroso-compound with hydroxyl-amine hydrochloride and alcohol in a reflux apparatus. It crystallises in white needles, melts at 294°, and sublimes without decomposition. When boiled with excess of alkali or with 50 per cent. sulphuric acid, it is converted into naphthalenedioxime anhydride, $C_{10}H_6{\ll}^N_N{>}0$

(Goldschmidt and Schmid, Abstr., 1884, 1327), which crystallises in needles, and melts at 78°. The formation of this compound proves that the hydroxynaphthoic acid melting at 216° is the 2 : 3-compound.

E. C. R.

Ethereal Salts of Sulphonic acids. By F. KRAFFT and A. ROOS (*Ber.*, **26,** 2823—2829).—It has been already shown (Abstr., 1892, 1219) that alkyl sulphonates are produced by the action of aromatic sulphonic chlorides on alcohols in the cold. The authors now find that when the sulphochlorides are heated with the alcohols in sealed tubes, the sulphonic acids and the ethers corresponding with the alcohols are formed. Alkyl chlorides are also obtained, due apparently, not to a direct decomposition, but to the reaction between the hydrogen chloride directly formed and the alcohol. The authors confirm Armstrong and Rossiter's observation (Proc., 1891, 184) with regard to the action of alcohol on 1 : 4-dibromonaphthalene-sulphonic chloride. When the latter is heated on the water bath

with an excess of alcohol, it is entirely converted after a short time into the free sulphonic acid. That hydrogen chloride plays no important part in the change, is shown by the fact that when ethylic 1 : 4-dibromonaphthalenesulphonate is heated with absolute alcohol in a sealed tube, the products are the free sulphonic acid and ethylic ether. A. R. L.

Thionaphthens. By L. GATTERMANN and A. E. LOCKHART (*Ber.*, **26**, 2808—2809).—*Thionaphthen*, $C_6H_4 <_S^{CH}>CH$, is obtained by adding a solution of the diazo-derivative of orthamidochlorocinnamene, $NH_2 \cdot C_6H_4 \cdot CH : CHCl$, to one of potassium xanthate in the cold, whereby the diazoxyxanthate separates; if the product be warmed on the water bath, nitrogen is evolved and an oil, probably $OEt \cdot CS \cdot S \cdot C_6H_4 \cdot CH : CHCl$, is formed. When this oil is boiled for several hours with alcoholic potash, it yields thionaphthen, together with other compounds; a cold alcoholic solution of picric acid is now added to the mixture, whereby the sparingly soluble picrate of thionaphthen separates in golden-yellow needles; it melts at 149°, and on decomposition with ammonia, yields thionaphthen. The latter is driven over with steam, and forms colourless plates, melts at 30—31°, resembles both naphthalene and naphthylamine in odour, and gives a red coloration with concentrated sulphuric acid.
A. R. L.

Orientation in the Terpene Series. By A. BAEYER (*Ber.*, **26**, 2861—2869).—Cases of cistrans-isomerism have not hitherto been observed in the terpene series, although the study of the hexahydrophthalic acids has rendered their existence probable. The author has found that the dihydrochloride and dihydrobromide of dipentene and terpin itself do exist in two forms, the series of lower melting point being looked upon by him provisionally as the cis-form.

Dipentene cis-dihydrochloride is formed when cineol or eucalyptol is treated with hydrogen chloride at the temperature of melting ice. It is a white, camphor-like mass, and melts at about 25°, whilst the already known trans-form melts at 50° (Wallach).

Dipentene cis-dihydrobromide is prepared by treating eucalyptol with a solution of hydrogen bromide in acetic acid at 0°. A mixture of the two isomerides is obtained from which the separate compounds may be isolated by dissolution in alcohol, and fractional precipitation with water. The cis-form crystallises in pointed plates melting at about 39°, whilst the already known trans-form crystallises in rhombic tablets, and melts at 64°.

The relative proportion of these two dihydrobromides formed by the treatment of the various compounds of the series with hydrogen bromide or phosphorus tribromide is shown in the following table.

		Dihydrobromide.	
		cis-	trans-
1. trans-Terpin	+ HBr	—	almost exclusively
2. Terpineol cryst.	+ HBr	—	,,
3. cis-Terpenhydrate	+ HBr	—	,,

		Dihydrobromide.	
		cis-	trans-
4. cis-Terpin	+ HBr	a little	much
5. Limonene	+ HBr	a little	much
6. cis-Terpin	+ PBr$_3$	about half	about half
7. Cineol	+ HBr	the greater portion	a little

Both forms yield the same dipentene, but different terpins. The cis-dihydrobromide, when treated successively with silver acetate and alcoholic potash, gives the well-known terpin, the hydrate of which melts at 117·5°. The trans-dihydrobromide, on the other hand, when similarly treated, gives a new *trans-terpin*, which crystallises without water and melts at 156—158°. It is readily soluble in alcohol, but only slightly in water, ether, or ethylic acetate, from which it separates in short prisms or six-sided tablets, with a strong, vitreous lustre. It boils at 263—265°, whilst Wallach found that the old cis-terpin boils at 258·5°. Since cineol yields almost exclusively the cis-dihydrobromide, it is most probably itself a cis-derivative, and the anhydride of the previously known cis-terpin. A trans-cineol has not yet been obtained.

It is to be observed that—(1) cis-terpin, when treated with hydrogen bromide, undergoes molecular change and yields the trans-dihydrobromide, whilst cineol, its anhydride, does not; and (2) that the molecular change takes place in the conversion of terpin into the dihydrobromide, whilst no molecular change occurs in the inverse production of terpin from the dihydrobromide. This apparently anomalous behaviour is probably to be explained by the intermediate formation of an unsaturated compound in those cases in which molecular change occurs. A. H.

Chrysin. By S. v. KOSTANECKI (*Ber.*, **26**, 2901—2305).—Chrysin, $C_{15}H_{10}O_4$, when boiled with alkali, yields phloroglucinol, benzoic and acetic acids, and also some acetophenone. It yields monalkyl ethers, which are insoluble in alkali. The monomethyl derivative is identical with tectochrysin.

A *diacetyl derivative*, $C_{15}H_8O_4Ac_2$, obtained by boiling it with acetic anhydride and anhydrous sodium acetate, crystallises in white needles, and melts at 185°.

The *sodium salt* of tectochrysin is obtained by adding sodium hydroxide to the alcoholic solution; it crystallises in intensely yellow needles, and is almost insoluble. *Acetylchrysin monomethyl ether*, $OMe\cdot C_{15}H_8O_3Ac$, crystallises in white, lustrous needles, and melts at 149°.

The above reactions of chrysin are most easily explained by assigning to it the formula $C_6H_2(OH)_2 {<}^{O-CPh}_{CO\cdot CH}$ [OH : OH = 1 : 3].

E. C. R.

Dry Distillation of Jalapin. By E. KLIMENKO and Y. BANDALIN (*J. Russ. Chem. Soc.*, **25**, 136—142).—Jalapin was distilled in portions

of 20 grams from a small glass retort, at as low a heat as possible. The chief products obtained were—

1. An aqueous liquid boiling at 102—103°. This proved to be a solution of acetic acid of constant boiling point.

2. A brown liquid passing over between 170° and 220°, which, after treatment with sodium carbonate, and decomposition of the sodium salt with hydrochloric acid and extraction with ether, yielded tiglic acid.

3. A liquid collected above 220°, which partially solidified in the receiver. The solid, after purification, was found to be palmitic acid.   J. W.

Constituents of Coto Bark. By O. Hesse (*Ber.*, **26**, 2790—2795).—A continuation of the discussion with Ciamician and Silber. Mixtures of " methylprotocotoïn " (" oxyleucotin "), and " methylhydrocotoïn " (" benzoylhydrocoton "), or of " isomethylhydrocotoïn." resemble " leucotin," both in appearance and melting point (Abstr., 1893, i, 417), but the melting point of leucotin is constant, whilst that of the mixture is not. The remainder of the paper deals with " paracotoïn," " bromoparacotoïn," " paracotoïnic acid," " cotoïn," and " dicotoïn."   A. R. L.

Colouring Matter of Cochineal. By W. v. Miller and G. Rohde (*Ber.*, **26**, 2647—2672).—Hlasiwetz and Grabowsky (*Annalen*, **141**, 329) considered that De la Rue's carminic acid (*Annalen*, **64**, 1) was a glucoside yielding on hydrolysis carmine-red and a sugar; the authors show, however, that this is incorrect, and that carminic acid is not altered in composition by boiling with dilute sulphuric acid. They have obtained 1·4 per cent. of tyrosine from cochineal extract, whereas de la Rue found only 0·4 per cent.

It has been pointed out by Will and Leymann (Abstr., 1886, 252), that α- and β-bromocarmin yield methyldibromohydroxyphthalic acid [Me : Br₂ : OH : (COOH)₂ = 1 : 4 : 6 : 5 : 2 : 3] on oxidation. The authors find that the last-named acid is formed, together with bromoform, when α-bromocarmin is warmed with an excess of soda solution; they consider, therefore, α-bromocarmin to be an indone derivative of

the constitution $C_6MeBr_2(OH)\overset{1\ 4,6}{\underset{}{}}\overset{5}{}<\overset{CO}{\underset{CO}{}}>CBr_2$ (compare Zincke, Abstr.,

1888, 291, 1198). Bearing in mind Zincke's observation, that indone derivatives are formed by the molecular degradation of halogenated derivatives of hydroxy-α-naphthaquinone, it seemed not improbable that β-bromocarmin, which contains in its molecule 1 atom of carbon less than α-bromocarmin, might belong to the latter class of compounds, especially as it bears a great resemblance to Diehl and Merz's bromhydroxynaphthaquinone (*Ber.*, **11**, 1066). This hypothesis is borne out by the fact that β-bromocarmin is convertible into α-bromocarmin (see below). When β-bromocarmin (1 mol.) is dissolved in a solution of sodium carbonate (2 mols.) and treated in the cold with bromine (1 mol.), the hydroxy-acid,

$$C_6MeBr_2(OH)\overset{1\ 4,6}{\underset{}{}}\overset{5}{}<\overset{C(OH)\cdot COOH}{\underset{CO\ \underline{\quad\quad}}{}}>CBr_2,$$
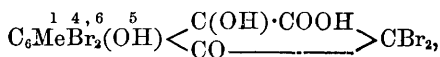
is formed. It crystallises with $3H_2O$, and melts at 106° or 208°, according as it is heated rapidly or slowly; if crystallised from ether, two melting points (somewhat higher) are also observed. When the hydroxy-acid is warmed with 50 per cent. acetic acid and bromine, it is converted into α-bromocarmin. These results show, therefore, that β-bromocarmin has the constitution represented by one of the formulæ

$$\begin{matrix} CBr{=}CMe \cdot C \cdot CO \cdot C \cdot OH \\ | \quad\quad || \quad || \\ C(OH){:}CBr{\cdot}C{\cdot}CO{\cdot}CBr \end{matrix} \text{ or } \begin{matrix} CBr{=}CMe \cdot C{\cdot}CO{\cdot}CBr \\ | \quad\quad || \quad || \\ C(OH){:}CBr{\cdot}C{\cdot}CO{\cdot}C{\cdot}OH \end{matrix}.$$

If β-bromocarmin is dissolved in aqueous alkali, and the warm solution is treated with zinc-dust, it is converted into the *quinol*,

$$C_6MeBr_2(OH){<}\begin{matrix}\overset{1\ 4,6\quad\ 5}{C(OH){:}C{\cdot}OH} \\ C(OH){:}CH\end{matrix}, \text{ which crystallises in almost colourless}$$

needles, and darkens without melting when heated. The *tetracetyl* derivative, $C_{19}H_{16}Br_2O_8$, melts at 206°. When the quinol is dissolved in alkali, and the solution is exposed to the air, a red salt separates; this, on treatment with acid, yields a substance which crystallises in yellow needles, melts at 263—265°, and resembles β-bromocarmin; when warmed with acetic acid and bromine, it is converted into α-bromocarmin.

The authors are unable to confirm Will and Leymann's observation (*loc. cit.*), that β-bromocarmin yields a colouring matter resembling carminic acid when treated with alkaline stannous chloride, and exposed to the air; the product is a yellowish-red compound, resembling the substance of melting point 263—265° mentioned above.

Carminic acid is, therefore, closely related to one of the two hydroxy-derivatives of methyl-α-naphthaquinone having the formulæ $C_{10}H_3Me(OH)_2O_2$

$$[Me : OH : O_2 : OH = 1' : 3' : 1 : 4 : 2, \text{ or } 1' : 3' : 1 : 4 : 3].$$
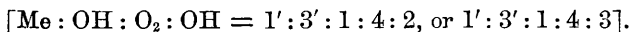
The authors' analytical values for carminic acid and those of De la Rue agree well, but they are about 10 per cent. lower in carbon than those required for a compound of the above formula; compared with a dihydrate of such a compound, which might be the analogue of leuconic acid or triquinoyl (Nietzki and Benckiser), the agreement is better, but even then not satisfactory. It is pointed out, however, that carminic acid has, up to the present, only been obtained in an amorphous state. The authors find also that ruficoccin yields α-bromocarmin when treated with bromine in acetic acid solution; hence it must be nearly related to carminic acid, and they no longer accept Liebermann and van Dorp's statement (*loc. cit.*) that it is an anthracene derivative.   A. R. L.

Instability of Colouring Matters containing Carotene. By M. GERLACH (*Bied. Centr.*, **22**, 786).—The fad·ng of dyes containing carotene is not due to light, but to the oxygen of the air, as the change takes place in darkness as well as in light, but the colour is permanent in light when oxygen is excluded; at the same time the change is assisted by light.   E. W. P.

Conversion of Indoles into Quinolines. By A. FERRATINI (*Gazzetta*, **23**, ii, 105—124).—This paper gives a detailed account of the work of which a short notice has already appeared (Abstr., 1893, i, 602).

Action of Phenylic Isocyanochloride on Derivatives of Phenylhydrazine. By M. FREUND and E. KÖNIG (*Ber.*, **26**, 2869—2874).—Phenylic isocyanochloride, NPh:CCl$_2$, is obtained by treating phenylthiocarbimide dissolved in chloroform with dry chlorine. It is a colourless oil, and boils at 205°.

Phenylphenylimido-oxybiazoline, $N<^{CH \cdot O}_{NPh \cdot C:NPh}$, is obtained by heating dry formylphenylhydrazine with phenylic isocyanochloride. It crystallises in concentric, white needles, melts at 99°, and is not altered by boiling with water or soda solution. The *hydrochloride* crystallises in white needles, melts at 185—186°, and is decomposed by water.

Formylamidodiphenylcarbamide, NHPh·CO·NPh·NH·CHO, is obtained by heating moist formylphenylhydrazine with phenylic isocyanochloride. It crystallises in leaflets or needles, melts at 164°, is a feeble base, and is not altered by boiling with dilute alcoholic potash. It is also obtained by evaporating on the water bath, an alcoholic solution of the preceding oxybiazoline mixed with concentrated hydrochloric acid.

Phenylmethylphenylimido-oxybiazoline, $N<^{CMe \cdot O}_{NPh \cdot C:NPh}$, is obtained from acetylphenylhydrazine in a similar way to the above oxybiazoline. It crystallises in white needles, melts at 75°, yields an oily hydrochloride, and, when boiled with alcoholic potash, yields a red solution which contains free phenylhydrazine. The *platinochloride* crystallises in tufts of shining needles, and melts at 92°.

Acetylamidodiphenylcarbamide, NHPh·CO·NPh·NH·COMe, is obtained in a similar way to the above formyl compound. It crystallises from absolute alcohol in needles, melts at 181°, and is a weak base.

Phenylimidodiphenyloxybiazoline, $N<^{CPh \cdot O}_{NPh \cdot C:NPh}$, is obtained by boiling benzoylphenylhydrazine with phenylic isocyanochloride and toluene. It crystallises in white needles, sinters at 102°, melts at 106°, and is insoluble in hydrochloric acid.

Phenylamidophenylimidophenylthiobiazoline, $N<^{C(NHPh) \cdot S}_{NPh \underline{\quad\quad} C:NPh}$, is obtained by warming diphenylthiosemicarbamide (m. p. 176°) with chloroform and phenylic isocyanochloride, and then decomposing with soda the hydrochloride thus obtained. It crystallises in white needles, and melts at 154°. The *hydrochloride* crystallises in pale yellowish-green, rhombic tablets, evolves hydrogen chloride at 140°, and then melts at 215°. The *nitroso-compound* is obtained in small, golden-yellow needles, melts at 110°, and is so unstable that it cannot be recrystallised.

Benzeneazophenylimidophenylthiobiazoline, $N<^{C(N:NPh)\cdot S}_{NPh \underline{\hspace{1.5em}} C:NPh}$, is obtained by warming phenylic isocyanochloride with a solution of diphenylthiocarbazone in chloroform. It crystallises in cherry-red needles, and melts at 180—181°. The *hydrazo-compound,* obtained by boiling it with a solution of ammonium sulphide in dilute alcohol, crystallises in white needles, and melts at 150°. E. C. R.

Derivatives of Oxybiazolone and Thiobiazolone. By E. König (*Ber.,* **26**, 2876; see also *Ber.,* **24**, 1178).—*Orthotolylphenyl-oxybiazolone,* $C_7H_7\cdot N<^{\underline{\hspace{1em}}N}_{CO\cdot O}>CPh$, crystallises from alcohol in needles, and melts at 120°.

Orthotolylphenyl-ψ-thiobiazolone, $C_7H_7\cdot N<^{\underline{\hspace{1em}}N}_{CS\cdot O}>CPh$, crystallises from light petroleum in pale yellow prisms, and melts at 96°.

Orthotolylamido-oxybiazolone, $C_7H_7\cdot N<^{\underline{\hspace{1em}}N}_{CO\cdot O}>C\cdot NH_2$, crystallises from a mixture of chloroform and light petroleum in interlacing needles, and melts at 131°.

Orthotolylamidothiobiazolone, $C_7H_7\cdot N<^{\underline{\hspace{1em}}N}_{CO\cdot S}>C\cdot NH_2$, is obtained from orthotolylthiosemicarbazide (m. p. 156°) and carbonyl chloride. It crystallises in needles, and melts at 278—279°. E. C. R.

Triazole Derivatives. By M. Freund and S. Wischewiansky (*Ber.,* **26**, 2877—2881).—Thiocarbamides of the type

$$R\cdot NH\cdot CS\cdot NH\cdot NH\cdot CS\cdot NHR,$$

when treated with carbonyl chloride, lose 1 mol. of hydrogen sulphide, and are converted into bases of the triazole series having the constitution $NHR\cdot C<^{N\underline{\hspace{0.5em}}NH}_{NR\cdot CS}$ or $NR:C<^{NH\cdot N}_{NR\cdot C\cdot SH}$.

Hydrazodicarbonthioamide, $NH_2\cdot CS\cdot NH\cdot NH\cdot CS\cdot NH_2$, is obtained by boiling hydrazine sulphate with ammonium thiocyanate; it melts at 208°. When dissolved in toluene and heated with carbonyl chloride at 150—160°, it yields a yellow, insoluble compound which does not melt at 290°, and gave on analysis C, 23·11—22·65; H, 2·47—2·68; N, 36·93; and S, 26·8 per cent. Hydrazodicarbonamide, when treated with carbonyl chloride under the same conditions, is decomposed with the formation of ammonium chloride.

Hydrazodicarbonthioallylamide, $N_2H_2\cdot(CS\cdot NH\cdot C_3H_5)_2$, is obtained by heating in a reflux apparatus hydrazine sulphate mixed with the theoretical quantity of sodium carbonate and a slight excess of allyl-thiocarbimide dissolved in alcohol. When heated with carbonyl chloride and toluene, hydrogen sulphide is eliminated, and a *base* of the composition $C_8H_{12}N_4S$ is formed. This base is also obtained by boiling the allylcarbamide with sodium carbonate or concentrated hydrochloric acid. It crystallises in interlacing needles, and melts at

147°.   The *hydrochloride* crystallises with $3H_2O$, and melts at 49°. The *platinochloride* is obtained as a crystalline, sparingly soluble precipitate, and does not melt at 280°.   The *nitroso-compound* crystallises in yellow leaflets, and melts at 105°.   When the base is heated with methylic iodide and alcohol, it yields the methyl compound $C_8H_{11}MeN_4S,HI$, which crystallises in leaflets, and melts at 167°. The *hydrochloride* of this last compound crystallises in leaflets, and does not yield a nitroso-derivative.

Hydrazodicarbonthiophenylamide, $N_2H_2 \cdot (CS \cdot NHPh)_2$, obtained in a similar way to the above allyl derivative, crystallises in white scales, and melts at 187°.   When heated with carbonyl chloride, it yields the compound $C_{14}H_{12}N_4S$, which melts at 239—240°.

<div align="right">E. C. R.</div>

Formazyl Methyl Ketone. By E. BAMBERGER and P. DE GRUYTER (*Ber.*, **26**, 2783—2786).—The compound of melting point 183°, obtained by the action of alcoholic ammonium sulphide on formazyl methyl ketone (*Abstr.*, 1892, i, 158), is *acetylamidrazone*,

$$NH_2 \cdot CAc\colon N_2HPh$$
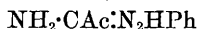
(compare this vol., i, 23).   The *ureïde*, $N_2HPh\colon CAc \cdot NH \cdot CO \cdot NH_2$, prepared by treating it with potassium cyanate, melts at 183°.   The *osazone*, $N_2HPh\colon CMe \cdot C(N_2HPh) \cdot NH_2$, obtained by treating acetylamidrazone or formazyl methyl ketone with phenylhydrazine, or boiling the former with dilute sulphuric acid, forms small, white needles, melts at 224°, and becomes reddish-violet on exposure to the air ; concentrated sulphuric acid dissolves it with an intense bluish-violet coloration, whilst alkalis colour its alcoholic solution red. The *sulphate* melts at 211° ; the *hydrochloride* melts at 114—115° apparently with dissociation.   When the osazone is heated with glacial acetic acid at 180°, *phenylamidomethylosotriazole*, $NPh{<}^{N\colon CMe}_{N\colon C \cdot NH_2}$, is formed ; it is volatile with steam, and melts at 73°.

Acetylamidrazone yields an *acetyl* derivative, $NHAc \cdot CAc\colon N_2HPh$, which forms yellowish-white, satiny needles, is insoluble in dilute mineral acids, melts at 143°, and, when heated with dilute acetic acid, is converted into *phenylacetylmethyltriazole*, $NPh{<}^{N = CAc}_{CMe\colon N}$, melting at 88—89°.   The latter gives a crystalline compound with sodium hydrogen sulphite, an *oxime* melting at 211—212°, and a *phenylhydrazone* which crystallises with 1 mol. of acetic acid, and melts at 128°, but loses the acetic acid, and becomes oily on exposure to the air.   A. R. L.

Formazyl Phenyl Ketone. By E. BAMBERGER and H. WITTER (*Ber.*, **26**, 2786—2790).—*Formazyl phenyl ketone*,

$$COPh \cdot C(N_2Ph)\colon N_2HPh,$$
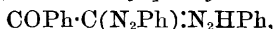
is formed, together with a smaller amount of Claisen's phenylazobenzoylacetone (*Abstr.*, 1888, 828), by the action of benzoylacetone or of benzoylacetic acid on diazobenzene in presence of free alkali ; it crystallises in red, felted needles of a metallic lustre, and melts

at 141—142°. The *silver* salt explodes when heated, and the *acetyl* derivative, $COPh \cdot C(N_2Ph){:}N_2AcPh$, melts at 154°.

α-*Phenyltriazyl phenyl ketone*, $C_6H_4{<}^{N{:}N}_{N{:}C \cdot COPh}$. is produced, together with aniline, by the action of concentrated mineral acids on formazyl phenyl ketone; it crystallises in golden-yellow bunches of needles, melts at 114°, and forms a hydrazone melting at 185°.

Benzoylamidrazone, $COPh \cdot C(N_2HPh) \cdot NH_2$, is formed, together with aniline, when formazyl phenyl ketone is reduced with alcoholic ammonium sulphide; it melts at 152°, and gives Bülow's reaction. The *acetyl* derivative melts at 143—156°, according to the rapidity with which it is heated, and also gives Bülow's reaction. When heated, the acetyl derivative yields *methylphenylbenzoyltriazole*, $NPh{<}^{N \,=\, C \cdot COPh}_{CMe{:}N}$, which crystallises in colourless, silky needles, and melts at 55·5°.　　　　　　　　　　　　　　　　　A. R. L.

Isoquinine and Nichine.

By E. LIPPMANN and F. FLEISSNER (*Monatsh.*, **14**, 553—558; compare Abstr., 1892, 81 and 83).—The authors confirm their previous statement (*loc. cit.*) as to the individuality of the base isoquinine, which melts at 185°, and which has been stated by Skraup (Abstr., 1893, i, 56) to be a mixture of pseudo-quinine and nichine.

Nichine may be obtained in largest yield by taking hydriodo-quinine, recently precipitated in a crude form by ammonia, and adding to it silver nitrate, in slight excess above that required to completely precipitate the iodine; after removing the excess of silver with hydrochloric acid, the base is precipitated with ammonia. Nichine forms a well characterised hydrate, $3C_{19}H_{24}N_2O_2 + 2H_2O$, which crystallises in needles, and melts at 70°. The anhydrous base melts at 130—132°. Its acid solutions have a marked fluorescence, and give the characteristic quinine reaction with chlorine water and ammonia. The *dihydrochloride*, $C_{19}H_{24}N_2O_2,2HCl$, forms small, granular crystals; the *acid sulphate* crystallises in long needles, and, like the *acid oxalate*, is very sparingly soluble in water and in alcohol.　　　　　　　　　　　　　　　　　G. T. M.

Relation between the Optical Rotary Power of Cinchonidine and its Salts: Influence of the Solvent on the Rotation.

By C. A. SCHUSTER (*Monatsh.*, **14**, 573—595).—Cinchonidine and its salts, including the hitherto unknown hydrobromide and hydriodide, are lævorotatory. In alcoholic solution, all the salts, with the exception of the sulphate, show a maximum rotation, for like concentration, in 50 per cent. alcohol, and a minimum rotation in absolute alcohol. In the case of the sulphate, the maximum rotation is also given in a solution of 50 per cent. alcohol, but the minimum rotation is given by the aqueous solution. The difference in rotatory power of the various cinchonidine salts in aqueous solution is exceedingly small, and very closely resembles that calculated for the base, the maximum divergence

being obtained when the base is united with some weak acid, such as acetic acid. This behaviour is in harmony with the Arrhenius' dissociation theory. Comparisons of the rotatory powers of the compounds of cinchonidine with the halogen acids show that the rotation diminishes with increase in the molecular weight, according to Guye's rule. G. T. M.

Alkaloïds of the Root of Corydalis cava. By M. FREUND and W. JOSEPHI (*Annalen*, **277**, 1—19; compare Abstr., 1892, 1366).—Corydaline, $C_{22}H_{27}NO_4$ (compare *loc. cit.*, also Dobbie and Lauder, Trans., 1892, 244 and 605).—The specific rotatory power of the base in chloroform solution is $[\alpha]_D = +300\cdot1$. The *hydrochloride* crystallises with $2H_2O$, and melts at 206—207°; and the *hydriodide* decomposes at 220°. When the methiodide is digested on the water bath with silver chloride and aqueous alkali, *methylcorydaline*, $C_{23}H_{29}NO_4$, is obtained; it crystallises from alcohol in colourless prisms, and melts at 112°; the *hydrochloride* crystallises with $6H_2O$. *Methylcorydaline methiodide*, $C_{23}H_{29}NO_4MeI$, melts at 195—196°; both it and the methochloride are stable towards alkalis, thus recalling the similar indifference of the methohalogen compounds of hydrohydrastinine (Abstr., 1891, 1519), and the authors consider it probable that corydaline also contains a hydrogenised isoquinoline nucleus, having a methyl group united to the nitrogen atom.

Bulbocapnine.—The formula previously assigned by the authors to this base (*loc. cit.*) is incorrect; their present analyses agree with the formula $C_{19}H_{19}NO_4$. The base crystallises from alcohol in rhombic, hemihedral prisms, $a : b : c = 0\cdot72700 : 1 : 0\cdot73682$; its specific rotatory power in chloroform solution is $[\alpha]_D = +237\cdot1$. The *hydrochloride*, *hydrobromide*, *hydriodide*, and *nitrate* are anhydrous, and decompose above 230°; the *acid sulphate* has the formula $C_{19}H_{19}NO_4,H_2SO_4 + 2H_2O$; and the *methiodide* crystallises from water in lustrous needles, and melts at 257°. A determination by Zeisel's method indicated the presence of a single methoxy-group in bulbocapnine. Bearing in mind Dobbie and Lauder's observation that corydaline contains four methoxy-groups, the relation of the two bases is, perhaps, $C_{18}H_{13}N(OH)_3\cdot OMe$ and $C_{18}H_{15}N(OMe)_4$.

Corycavine, $C_{23}H_{23}NO_5$ (see *loc. cit.*).

Corybulbine is the name given by the authors to a base isolated from commercial corydaline (*loc. cit.*); it differs from Dobbie and Lauder's corytuberine (Trans., 1893, 485) in being insoluble in water. Lack of material precluded the determination of its formula. The authors leave the further development of the subject to Dobbie and Lauder. A. R. L.

Organic Chemistry.

Dinitromethane. By P. DUDEN (*Ber.*, **26**, 3003—3011).—*Dinitromethane*, $CH_2(NO_2)_2$, is obtained as potassium derivative by the action of dibromodinitromethane on arsenious anhydride, potash, and water at low temperatures; after remaining for some time, the reaction is completed by heating in a reflux apparatus; the product is then suspended in water and ether and decomposed by dilute sulphuric acid; on evaporating the ethereal solution at a low temperature, the dinitro-compound remains as a yellow oil, having a characteristic acid odour. It rapidly decomposes at ordinary temperatures, even in a sealed tube, and does not solidify at $-15°$; in ethereal or benzene solution, it is stable, and is volatile with benzene vapour, and also with steam. By the action of bromine water on dinitromethane, the dibromo-derivative is regenerated; with hydroxides, carbonates, sulphites, and nitrites, metallic derivatives are formed, carbonic anhydride, sulphurous anhydride, and nitrous acid being liberated. The *potassium* derivative, $CH(NO_2)_2K$, crystallises from water in pale yellow, monoclinic crystals; the aqueous solution is neutral; by the action of concentrated or dilute acids at ordinary temperatures, decomposition takes place, with evolution of nitrous fumes; on heating it to about 205°, potassium carbonate, water, carbonic anhydride, nitric oxide, and nitrogen are formed. Villiers' statement that it is unstable is incorrect; when pure, it undergoes no change on exposure to air; in a closed vessel, a slight, superficial decomposition takes place. The *ammonium* derivative crystallises from alcohol-ether in slender, pale yellow needles, which explode at about 105°. The *phenylhydrazine* compound forms intensely yellow needles, and melts at 101° with decomposition. The *copper* derivative is pale green, and readily decomposes in aqueous solution. The *barium* derivative, $(CHN_2O_4)_2Ba + 2H_2O$, crystallises in pale yellow needles; on heating, it becomes anhydrous and darkens, and finally explodes. The *silver* derivative, $CH(NO_2)_2Ag$, crystallises in lustrous, yellowish-green plates, and decomposes rapidly on exposure to light, on boiling with water, or on heating to 135°. Dinitroethane and dinitropropane are formed by the action of methylic iodide and ethylic iodide respectively on the silver derivative at ordinary temperatures. By the action of nitrous acid on potassium dinitromethane, *isonitrosodinitromethane*, $NOH:C(NO_2)_2$, appears to be formed; it is extremely unstable, dissolves in ether with a blood-red colour, and forms a sodium and a silver derivative, neither of which could be completely freed from nitrite. Ammonia is eliminated by the reduction of dinitromethane in acid solution, but, on treatment with sodium amalgam at 0°, methylazaurolic acid, CH_2N_2O, is formed. Potassium dinitromethane and diazobenzene hydrochloride in glacial acetic acid solution yield a compound which has the formula $C(NO_2)_2(NP_2h)_2$, and crystallises in orange-red needles, melting at 75° with decomposition; it is readily soluble, and decomposes on boiling, or by the action of alkalis.   J. B. T.

Synthesis of Nitroparaffins. By I. BEVAD (*J. pr. Chem.*, [2], **48**, 345—383; compare Abstr., 1893, i, 242, 382).—The zinc alkylides react with the halogen- nitro-derivatives of the hydrocarbons displacing the halogen atom (1) by an alkyl group, (2) by hydrogen, and (3) by both alkyl group and hydrogen. The first reaction produces secondary and tertiary nitro-compounds more complex than those treated (see Abstr., 1893, i, 242); the second results in the formation of the same primary or secondary nitro-compound, whose halogen derivative was treated; whilst the third only occurs with those compounds which contain not fewer than 2 halogen atoms, and produces primary and secondary nitro-compounds more complex than those treated.   A. G. B.

Action of Reducing Agents on Potassium Nickelocyanide. By T. MOORE (*Chem. News*, **68**, 295).—The author has investigated the nature of the red coloration produced when a strip of zinc is immersed in a solution of potassium nickelocyanide containing ammonium chloride and ammonia; the colour is very fugitive, and oxygen and zinc compounds aid its destruction. By treating the nickelocyanide with sodium amalgam in an atmosphere of hydrogen, a deep red solution is readily obtained, which gives, amongst others, the following reactions:—With silver nitrate, a heavy, black precipitate of metallic silver; with mercuric chloride, a grey precipitate; with lead acetate, a black precipitate, insoluble in potassium hydroxide or acetic acid, decomposed on drying, leaving yellow lead oxide; with bismuth nitrate, a black precipitate; with arsenious anhydride, a deep brown precipitate; gold chloride is slowly reduced. The solution is, moreover, decolorised by permanganate, dichromate, hydrogen peroxide, &c. When acidified, it yields an orange-yellow, flocculent precipitate, which, after filtration and washing with cold water, dissolves in alkalis to a red solution; the precipitate darkens and becomes dirty blue in the air, and decomposes completely on drying, even in hydrogen, yielding apparently a mixture of nickel oxide and cyanide. The instability of the substance has, so far, prevented its being submitted to analysis, but experiments indicate that the red solution absorbs 2 atoms of oxygen for every 3 atoms of nickel present.   D. A. L.

Oxidation of Potassium Cobaltocyanide. By T. MOORE (*Chem. News*, **68**, 295—296).—The equation $2K_4COCy_6 + 2H_2O + O = K_6C_2O_2Cy_{12} + 2KHO + H_2O$ has been regarded as representing the conversion of potassium cobaltocyanide into the cobalticyanide in the presence of free hydrocyanic acid and with access of air. On adding a mixture of sodium hydroxide and potassium cyanide to a solution of cobalt and agitating with air until absorption ceases, the author finds that the liquid becomes deep red-brown, and that oxygen is taken up in quantities varying between 8000 to 9600 c.c. per 59 grams of cobalt, instead of 5600 c.c. as required by theory. In similar experiments, with the sodium hydroxide omitted and the liquid strongly acidified instead, the solution became yellow, and oxygen was absorbed to the extent of 7450 to 7516 c.c. per 59 grams of cobalt. As no bye-products were observed, and as these oxidised solutions evolve oxygen

on boiling, it is suggested that there are higher cobalticyanides than the one indicated above. D. A. L.

Rate of Etherification of Hydrogen Fluoride. By M. MESLANS (*Compt. rend.*, **117**, 853—856).—The action of hydrogen fluoride on alcohol at about 200° (Abstr., 1893, i, 186) is at first rapid, but after four hours becomes slower, and attains its maximum in 10 hours. The temperature exerts great influence on the rate of change; at 170° the velocity of etherification is 10 times as great, and at 190° it is 20 times as great, as at 140°.

When the alcohol is in excess, no methylic fluoride is formed, and the sole product is ordinary ether. An excess of hydrogen fluoride, on the other hand, greatly accelerates the change, and the velocity of etherification is 60 times as great with a mixture of 4 mols. of the acid and 1 mol. of alcohol as it is with a mixture in equivalent proportions.

Thermal disturbances indicate the existence of stable alcoholates of hydrogen fluoride, and it would seem that when the alcohol is in excess, a part combines with the hydrogen fluoride to form stable alcoholates, whilst the remainder acts on the ethylic fluoride that is formed, and produces ordinary ether, whereas, when the hydrogen fluoride is in sufficient excess, no alcohol remains uncombined, and the secondary reaction does not take place. No ether is formed when 4 mols. of the acid are mixed with 1 mol. of alcohol, and with lower proportions of the acid the apparent velocity of etherification is the difference between the real velocity and the velocity of the secondary reaction.

The presence of water greatly reduces the rate of etherification, but some change takes place at 220°, even when 2 mols. of water are present for each mol. of hydrogen fluoride. C. H. B.

Electrolytic Oxidation of Glycerol. By W. E. STONE and H. N. McCOY (*Amer. Chem. J.*, **15**, 656—660).—A current of less than 0·3 ampère from one or two dichromate cells was passed between platinum electrodes placed in 10 per cent. aqueous glycerol, in which various inorganic substances were dissolved to lessen the resistance.

With dilute sulphuric acid or sodium nitrate (0·1 per cent.), the temperature rose, and the liquid, which in the latter case soon became acid, acquired the power of reducing alkaline copper tartrate in the cold, and yielded the rosaniline reaction for aldehydes; glycerose-aldehyde was, therefore, probably formed, and subsequently polymerised into glycerose. In the first case, an odour of acraldehyde was ultimately noticeable.

With a small quantity of sodium hydroxide, a yellow or yellowish-brown colour was first produced, probably due to the presence of a hexose, and after some hours the solution became acid in reaction; the acid in one case corresponding with as much as 80 per cent. of that theoretically producible from the glycerol. The solution reduced alkaline copper tartrate in the cold, and further, on boiling, showing the presence of a hexose. No odour of acraldehyde was perceptible.

When, the alkalinity of the solution was maintained, and the

i 2

current passed for several days, the power of reducing alkaline copper tartrate in the cold was at length lost, although, on boiling, a much more powerful reduction was obtained. The presence of a hexose was confirmed by the preparation of its osazone, which melted at 200° (m. p. d-glucosazone, 204—205°), and by its resolution into carbonic anhydride by fermentation with yeast.

An unsuccessful attempt was made to prepare the optically active modification of glyceric acid from one and the same portion of the inactive acid.   Jn. W.

Acetyl and Benzoyl Derivatives of Pentoses. By W. E. Stone (*Amer. Chem. J.*, **15**, 653—656).—*Tetracetylxylose*, $C_5H_6O_5Ac_4$, is prepared by heating xylose with acetic anhydride and fused sodium acetate. It crystallises in fine needles, melts without decomposition at 123·5—124·5°, and has a bitter taste. The specific rotatory power in anhydrous alcoholic solution is $[\alpha]_D = -25\cdot43°$, without multirotation. It is resolved by acid hydrolysis into its proximate constituents.

Tetracetylarabinose is prepared in a similar manner. It forms a thick syrup which solidifies when immersed in a mixture of solid carbonic anhydride and ether, and afterwards melts at $-7\cdot6°$. The specific rotatory power in anhydrous alcoholic solution is $[\alpha]_D = +26\cdot39°$. Its taste and its behaviour towards acid hydrolytic agents resemble that of its isomeride.

Attempts to prepare the corresponding benzoyl derivatives yielded crystalline substances having constant melting points (164—165° and 68—69°), but compositions agreeing with those of no single derivative; they are probably mixtures.   Jn. W.

Constitution of Glucose and the Glucosides. By L. March-lewski (*Ber.*, **26**, 2928—2930).—The author has previously shown (Trans., 1893, 1137) that the constitution of the glucosides may readily be explained by the help of Tollens' or other similar formula for glucose; no evidence was, however, adduced to show with which carbon atoms the oxygen atom present in the "ethylene oxide" form is combined. Inasmuch as the glucosides do not behave as aldehydes under any conditions, it is probable that the residue combined with the glucose is united with the carbon atom from which the aldehyde group of the original glucose is produced; and, further, as a second phenylhydr-azine residue may be combined with the carbon atom next to the aldehyde group in glucose, but not in the glucosides, it seems probable that the atom complex of this carbon atom has also undergone alteration. From this, the author concludes that the constitution of the glucosides is represented by the formula $O<\begin{matrix} CH\cdot[CH\cdot OH]_3\cdot CH_2\cdot OH \\ CH\cdot OR \end{matrix}$

As evidence against the supposition that the radicle displaces the hydrogen of one of the alcohol groups, the author adduces the fact that an aqueous solution of sodium glucosate is totally unaffected by phenylhydrazine.   H. G. C.

The Sugar of Phlorizin. By O. Hesse (*Annalen*, **277**, 302—304).—The author defends his remarks (*Annalen*, **172**, 356) that the

sugar (phlorose) from phlorizin is distinct from glucose (dextrose), despite the observations of Rennie (Trans., 1887, 634), Fischer (Abstr., 1888, 590), and Schunk and Marchlewski (Abstr., 1893, i, 384). On extracting, with methylic alcohol, the sample of sugar which was originally faintly yellowish but which after 15 years had become brown, glucose was obtained from the extract. Even this fails to convince the author that the original sugar is identical with glucose; he admits merely that phlorose is capable of being converted into glucose, but whether or not the change is brought about by the agency of lower organisms cannot be said.

<div align="right">A. R. L.</div>

Chloralose. By M. HANRIOT and C. RICHET (*Compt. rend.*, **117**, 734—737).—Chloralose (Abstr., 1893, i, 247) melts at 187°, and dissolves in alcohol, but is only slightly soluble in water or ether. Its boiling aqueous solution reduces neither ammoniacal silver nitrate nor Fehling's solution. Acids are without effect on it, but alkalis change the colour of the hot solution to brown. Chloralose is not affected by nascent hydrogen from sodium amalgam. With acids and acid chlorides, it yields di- and tetra-substitution derivatives, *tetracetylchloralose*, melting at 145°, and *tetrabenzoylchloralose* crystallising in prisms melting at 138°. Oxidation converts chloralose, with evolution of carbonic anhydride, into *chloralic acid*, $C_7H_9Cl_3O_6$, which crystallises in anhydrous needles melting at 212°, soluble in alcohol or ether, but only slightly soluble in water.

All these derivatives of chloralose are without physiological activity.

Parachloralose (*loc. cit.*) is insoluble in most reagents, melts at 227°, and sublimes if heated slowly. Like chloralose, it is not affected by hydroxylamine, phenylhydrazine, or dilute acids, but it is very slowly attacked by boiling solutions of alkalis. With acids and acid chlorides, it yields di- and tetra-derivatives; *tetracetylparachloralose* crystallises in long needles melting at 106°, and boiling at about 250° under a pressure of 25 mm. When oxidised, parachloralose yields carbonic anhydride and *parachloralic acid*, which crystallises with $2H_2O$ in efflorescent tables melting at 202°, and very soluble in alcohol or ether, but only slightly so in cold water.

These properties indicate that neither chloralose nor parachloralose have the aldehyde functions of glucose and chloral. They cannot be regarded as ethereal salts of glucose, and it would seem that they have the following constitution.

$$O< \begin{array}{l} CH \cdot CH(OH) \cdot O \cdot CH \cdot CCl_3 \\ CH \underline{\qquad\qquad} C(OH) \cdot CH(OH) \cdot CH_2 \cdot OH \end{array}$$
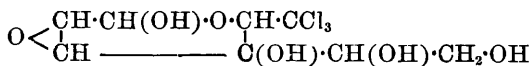
and $O< \begin{array}{l} CH \cdot CH(OH) \cdot C(OH) \cdot CCl_3 \\ CH \underline{\qquad\qquad} C(OH) \cdot CH(OH) \cdot CH_2 \cdot OH \end{array}$, although the position of the anhydric oxygen is somewhat uncertain.

<div align="right">C. H. B.</div>

Decomposition Products of Calcium Sucrate. By E. O. v. LIPPMANN (*Ber.*, **26**, 3057—3059).—A sample of calcium sucrate which had been preserved for five years was found to contain no

sugar; the lime was combined with carbonic, formic, acetic, and oxalic acids. Another sample of calcium sucrate, which had been preserved for two years, was treated with boric acid suspended in alcohol; the alcoholic solution yielded an acid syrup from which crystals were obtained, and identified by the author as acetonedicarboxylic acid (m. p. 136°).   E. C. R.

Decomposition Products of Cane Sugar. By E. O. v. LIPPMANN (*Ber.*, **26**, 3059—3061).—During the preparation of sugar-candy from pure white crystallised sugar, the mass sometimes becomes faintly acid, owing to the formation of decomposition products. An examination of the product showed the presence of a small quantity of a fruity ether and a dimethylfurfuran, C_6H_8O, which melts at 94°. Trihydroxybutyric acid and a small quantity of *trihydroxyglutaric acid*, $C_5H_8O_6$, were separated. The latter melts at 125°, and is dextrorotatory, $\alpha_{18}^D = 20.8°$. A syrupy acid was also obtained, which is probably identical with the hexepinic acid described by Maumené, and, finally, small quantities of catechol and protocatechuic acid.
                                                           E. C. R.

Carbohydrates Soluble in Water obtained from Malt and Barley. By G. DÜLL (*Chem. Zeit.*, **17**, 67—68 and 100).—Jalowetz came to the conclusion that the optical and reducing properties of cold water malt extract are to be attributed to the presence of dextrin and glucose (dextrose). The author extracts malt meal with boiling 80 per cent. alcohol for five hours, distils off the alcohol, takes up the residual syrup with water, and dialyses the solution. The grains, after being boiled with 80 per cent. alcohol, are extracted with cold water, and the solution submitted to dialysis. In this way it is shown by the optical rotation, the copper test, and the phenylhydrazine reaction, that the carbohydrates saccharose and invert sugar are present along with a gum (galactoxylan, and perhaps other gums), and besides these there are inorganic matter, proteïds, fat, choline, &c. (compare also Kühnemann, *Ber.*, **8**, 202 and 307; Kjeldahl, *Zeit. ges. Brauw.*, [2], **4**, 447). This applies both to air-dried and kiln-dried malt. There is no doubt that kiln-dried malt contains ready-formed invert sugar, and the author shows that the same is true of green malt, for when the latter is extracted with 0·2 per cent. ammonia, which arrests the action of the saccharose-hydrolysing enzyme, the presence of which Kjeldahl has recognised, the solution contains invert sugar.

Experiments with barley showed that it contained a non-reducing sugar yielding phenylglucosazone; the author therefore concludes that the only soluble carbohydrate present in barley besides the gum is saccharose. The aqueous extracts of barley generally gave the choline reaction.   A. R. L.

Note.—The author makes no reference to the well-known experiments of O'Sullivan on the sugars of cereals and germinated grain. It is especially surprising that the author fails to notice the fact that O'Sullivan has conclusively proved the presence of raffinose in barley (*Trans.*, 1886, 70). It is quite conceivable that the presence of

raffinose might escape detection by the osazone test, or it may be that raffinose is not an invariable constituent of barley.

A. R. L.

Starch. By C. SCHEIBLER and H. MITTELMEIER (*Ber.*, **26**, 2930— 2937).—In this paper, the authors reply to the recent communication of Lintner and Düll on the same subject (this vol., i, 5), pointing out that the results there detailed have, in some cases, already been described by the authors (Abstr., 1891, 33). They further do not agree with the theory proposed by Lintner and Düll, and devote the chief portion of the paper to an extension of their own theory as to the constitution of starch and the dextrins.

According to this there is no difference in principle between the constitution of starch and the dextrins, and that of the bioses such as cane sugar and maltose, and of the trioses such as melitriose, the dextrins and starch simply containing a much larger number of glucose residues in the molecule. The combination between two glucose molecules to form a biose may take place in two ways, according as either one or both of the carbonyl groups take part in the combination; in the former case, the compound formed has still the properties of an aldehyde, but not in the latter; this is exemplified in the cases of maltose and cane sugar. The former method of combination the authors term the monocarbonyl linking, and the latter the dicarbonyl linking.

In the case of starch, the glucose residues are all combined by dicarbonyl linkings, and do not therefore reduce Fehling's solution or react with phenylhydrazine. When treated with acids or ferments such as diastase, the first action is the hydrolysis of the starch molecule at one of the dicarbonyl linkings, yielding two molecules, each of which contains an aldehyde group, that particular glucose residue being connected with the remainder of the molecule by a monocarbonyl linking. These new substances form the dextrins, and as the hydrolysis of the starch molecule probably takes place simultaneously at several of the dicarbonyl linkings, a number of dextrins are simultaneously formed; by the further action of the ferment on these, however, they are split up into dextrins of smaller molecular weight, and, finally, when invertase is employed, into maltose; with acids, however, the hydrolysis goes further, and the whole is converted into glucose. The process is in fact similar to that observed in the case of melitriose, which is resolved first into melibiose and fructose, the former being in turn resolved into glucose and galactose (Abstr., 1890, 226, 1085). H. G. C.

Crystallisation of Cellulose. By E. GILSON (*Chem. Centr.*, 1893, ii, 530).—Under the term "cellulose," the author includes the carbohydrates of the membrane which are insoluble in dilute acids or alkalis, but soluble in sulphuric acid, and which are coloured blue by iodine in presence of concentrated sulphuric or phosphoric acid.

The author finds that if sections of cellular tissue are allowed to remain for a time in contact with Schweizer's reagent, then washed carefully first with ammonia and then with water, so that the copper compound dissolves gradually and the cellulose is precipitated slowly,

the latter is found in the interior of the cells in the form of nodular or arborescent crystals. These are insoluble in dilute acids and alkalis, but soluble in concentrated sulphuric acid, and show also the other characteristics of cellulose. To obtain the crystals certain precautions are necessary, one of these being the complete removal of starch before treating the section with Schweizer's reagent. The reaction has been successfully carried out with a large number of phanerogams and cryptogams. Objects such as the seed grains of *Coffea arabica*, *Phytelephas macrocarpa*, and *Strychnos nux vomica*, which contain reserve cellulose, show plainly the presence of two different substances in the membrane, one of which is coloured blue by iodine and zinc chloride, and can be obtained crystalline in the above manner; the other is amorphous and gives no coloration with iodine. Cotton-wool, wood, and tunicin may likewise be partially converted into crystals.

The author concludes that all membranes which are coloured by ammonia and zinc chloride can be in part obtained crystalline by the above treatment, and that only the portion which is thus coloured can be crystallised. The crystalline product has always the same appearance and properties, and appears therefore to be a distinct compound. All membranes contain cellulose, together with a considerable amount of other substances which are not coloured by the above reagent; whilst reserve cellulose consists of a mixture of the crystallisable cellulose with other carbohydrates. As the cellulose always crystallises on the interior of the cells, it must occupy the inner portion of the membrane, and when dissolved in Schweizer's reagent it diffuses very little, if at all, through the membrane. This observation affords an explanation of the fact that cellulose cannot be completely dissolved by Schweizer's reagent, and also of the manner in which Fremy was led to believe in the existence of a metacellulose, which is only soluble in the reagent after treatment with acids, for the acid dissolves or attacks the other constituents of the membrane, and allows the reagent free access to the cellulose hitherto held in the interior of the cells.

To obtain the cellulose in larger crystals, a solution of the pure substance in ammoniacal copper oxide is allowed to remain in a loosely-closed vessel; the ammonia slowly escapes, and cellulose and copper oxide are precipitated. The latter is removed by washing with hydrochloric acid and water, when the celluose remains in nodular crystals; on treatment with acids, it yields glucose as the sole product of hydrolysis. The mannosocellulose of Schulze is a mixture of cellulose with another carbohydrate for which the author proposes the term *paramanan;* this may also be obtained in the form of nodular crystals.

The membrane of all vegetable cells with the exception of the fungi appears to contain cellulose, which occurs in the free state. In the case of woody membranes, however, it is probably in combination with another hydrocarbon or allied compound.   H. G. C.

Oxidation of Aliphatic Aldehydes and Ketones by Nitric acid. By R. BEHREND and J. SCHMITZ (*Annalen*, **277**, 310—339).—

This paper commences with a bibliographical *résumé* of the subject. A preliminary account of the experiments on the action of nitric acid on acetone has already been published (compare Abstr., 1893, i, 303). The yellow oil thus obtained is decomposed when boiled with water yielding nitrous oxide, carbonic anhydride, formic, acetic, and oxalic acids, and hydrogen cyanide. Chloromethylglyoxime, obtained by warming chlorisonitrosoacetone with hydroxylamine hydrochloride (*loc. cit.*), melts with decomposition at 182—183°. Nitrosoxylmethyl-glyoxime, $NOH{:}CMe{\cdot}C(NOH)O{\cdot}NO$ (*loc. cit.*), obtained by treating an aqueous solution of the yellow unstable oil with hydroxylamine hydrochloride, when oxidised with nitric acid of sp. gr. 1·37 saturated with nitrous acid, gives a *compound* $C_3H_3N_3O_4$, which crystallises from aqueous alcohol in colourless, brittle plates, and melts at 66—67°; when heated with alcoholic potash, it dissolves, forming a yellow solution having the odour of peppermint. Its constitution is probably

$$\begin{matrix} CMe{\cdot}C{\cdot}NO_2 \\ \| \quad\ \| \\ NO{\cdot}ON \end{matrix}$$

, that is, it belongs to the class of oxime peroxides first prepared by Koreff (Abstr., 1886, 363), and subsequently studied by Hollemann (Abstr., 1888, 275; 1889, 49) and by Angeli (Abstr., 1891, 890 ; 1892, 1198; 1893, i, 310, 355). The compound of melting point 188—191°, obtained by treating nitrosoxylmethylglyoxime with a solution of sodium hydrogen carbonate, is shown, by the cryoscopic method, to have a molecular weight corresponding with the formula $C_6H_8N_4O_4$. If this is treated with nitric acid saturated with nitrous acid, a *compound* $C_3H_3N_3O_5$ is obtained, which melts at 113·5—115°.

When paraldehyde is oxidised with nitric acid according to De Forcrand's directions (*Bull. Soc. Chim.*, [2], **41**, 242), and the product is distilled under diminished pressure until its volume is reduced to one-fourth, formic and acetic acids, together with unaltered paraldehyde and a small quantity of formaldehyde, pass over, whilst on distilling the residue at the ordinary pressure glyoxal passes over.

In conclusion, the authors confirm Ljubavin's observation that the production of glyoxaline from ammonia and glyoxal depends on the initial formation of formaldehyde, which condenses with the ammonia and glyoxal. In the preparation of glyoxaline from glyoxal and ammonia, it is therefore advisable to add formaldehyde.

<div style="text-align:right">A. R L.</div>

Derivatives of Acetylacetone. By C. U. ZANETTI (*Gazzetta*, **23,** ii, 299—312).—Knorr (Abstr., 1887, 275) obtained 3 : 5 : 2 : 4-dimethyldiacetylpyrroline by reducing a mixture of ethylic nitroso-acetoacetate and ethylic acetoacetate. The author obtains the same pyrroline derivative by reducing with zinc dust the product of the action of potassium nitrite (1 mol.) on acetylacetone (2 mols.) in acetic acid solution; its *aurochloride*, $C_{10}H_{13}O_2N,HAuCl_4$, crystallises in small, yellow needles, which begin to decompose at 70° and melt at 120—130°.

3 : 5 : 2 : 4-*Dimethyldicinnamylpyrroline*, $C_{24}H_{27}O_2N$, is obtained by the action of benzaldehyde on the above diacetyl derivative in alkaline solution; it forms small needles melting at 215—216°.

Nitrosoacetylacetone, $CAc_2:NOH$, is an intermediate product in the formation of dimethyldiacetylpyrroline, and is isolated by dissolving acetylacetone in the minimum quantity of 12 per cent. potash, cooling with ice, adding the calculated quantity of potassium nitrite, and then, gradually, a slight excess of dilute sulphuric acid. Ether extracts the nitroso-derivative from the solution; it is ultimately obtained in pearly, flattened needles, or scales, which melt at 75°. It is very soluble in water, alcohol, or ethylic acetate, but only sparingly in benzene or light petroleum. It has a marked, although somewhat transient, antipyretic action on the animal system, and toxic symptoms are observed on administering a dose of 0·2 gram per kilo. of body weight. With hydroxylamine, it yields a product which seems to be a mixture. On reducing nitrosoacetylacetone with zinc dust in acetic acid solution in the cold, *dimethyldiacetaldine*, (?) $C_{10}H_{12}N_2O_2$ is obtained; it forms yellow needles melting at 101—102°, and acts as a feeble base. If the reduction proceeds at a high temperature, a liquid product is obtained which gives an unstable *platinochloride*; the author proposes to examine these reactions later.

Symmetrical tetracetylethane (compare Harrow, *Annalen*, **201**, 144) may be prepared by adding an ethereal solution of iodine to an ethereal solution of sodioacetylacetone, filtering, removing the sodium iodide by treatment with water, and crystallising the residue from acetic acid. On boiling tetracetylethane with concentrated hydrochloric acid, it yields *dimethyldiacetylfurfuran*, $\begin{matrix} CAc:CMe \\ CAc:CMe \end{matrix}>O$; this crystallises in long, waxy needles melting at 62·5°.

3 : 4 : 2 : 5-*Dimethyldiacetylpyrroline*, $\begin{matrix} CAc:CMe \\ CAc:CMe \end{matrix}>N$, is prepared by boiling tetracetylethane with ammonium acetate and acetic acid; it separates on the addition of alkali, and crystallises from hot water in opaque, white needles melting at 180—181°. It is readily soluble in alcohol or boiling water, but only sparingly in ether or ethylic acetate. It behaves as a feeble base, yielding a *hydrochloride* which crystallises in white needles; this is decomposed by water and gives off hydrogen chloride in a vacuum. The *aurochloride*,

$$C_{10}H_{13}O_2N,HAuCl_4$$
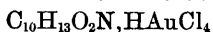
crystallises in yellow needles, and begins to decompose at 100°. A list of reactions of the base is given. A crystalline *hydrobromide* separates from the solution of the base in fuming hydrobromic acid; on adding bromine to the solution, however, an unstable *perbromide*, $C_{10}H_{13}O_2N,HBr,Br_2$, separates as a reddish mass, which yields the pyrroline when treated with sodium carbonate.

3 : 5 : 2-Dimethylacetylpyrroline is soluble in concentrated hydrochloric acid, and yields a fairly stable, yellow, crystalline *aurochloride*, $C_8H_{14}ON,HAuCl_4$. 2-Acetylhomopyrroline is moderately soluble in hydrochloric acid; its *aurochloride* forms minute needles and is less stable than the preceding one. 2 : 5-Diacetylpyrroline is very sparingly soluble in hydrochloric acid, and yields an *aurochloride* which is decomposed by water.

On treating a hot alkaline solution of acetylacetone with hydrazine

sulphate, 3 : 5-dimethylpyrazole is deposited. Acetylacetone reacts with benzaldehyde, giving a mixture of several cinnamyl derivatives; it is perhaps possible to separate these by taking advantage of their behaviour towards phenylhydrazine. **W. J. P.**

Condensation of β-Diketones with Carbamide, Guanidine, and Thiocarbamide. By P. N. EVANS (*J. pr. Chem.*, **45**, 489—517). —*Acetylacetonecarbamide*, $CO<^{N:CMe}_{N:CMe}>CH_2$, is obtained, as a salt, by the condensation of acetylacetone and carbamide (equal molecules) with sulphuric or hydrochloric acid. The *hydrochloride* crystallises in rectangular plates, and does not yield ammonia when boiled with concentrated sodium hydroxide. It gives no precipitate with platinic chloride. When treated with diazobenzene chloride and sodium acetate, it gives an orange, crystalline precipitate which quickly turns dark red; this compound is a powerful dye. The *sulphate*, $C_6H_8N_2O,H_2SO_4$, forms thick, transparent crystals, and melts at 209°. Acetylacetonecarbamide is most easily obtained by treating the sulphate with barium carbonate, evaporating the filtrate to dryness, and extracting with benzene. It crystallises from water in short, thick prisms, melts at 198°, and has both basic and weak acid properties. It is not altered by treatment with nitrous oxide or acetic chloride. The *silver salt*, $C_6H_7N_2OAg$, was obtained; the *mercury salt*, $C_6H_6N_2OHg$, is a yellow precipitate. On bromination, a *derivative*, $C_6H_{10}N_2O_3Br_2$ $(= CO<^{NBr·CMe(OH)}_{NBr·CMe(OH)}>CH_2?)$, is obtained; it crystallises in white, flocculent crystals, turns grey at 90°, blackens at 143—145°, and dissolves in ammonia.

Diurimidiacetylacetone, $CH_2(CMe:N·CO·NH_2)_2$, is obtained by the condensation of acetylacetone with 2 mols. of carbamide. The *hydrochloride*, $C_7H_{12}N_4O_2,HCl$, crystallises in slender, colourless needles, melts at 180°, does not give a precipitate with platinic chloride, and easily yields ammonia when heated with potassium hydroxide. When heated with silver oxide, it yields carbamide and acetylacetonecarbamide. A molecular compound of the sulphates of diurimidoacetylacetone and carbamide, $C_7H_{12}N_4O_2,CH_4H_2O,H_2SO_4$, crystallises in aggregates of slender needles, and melts at 142°. Diurimidoacetylacetone, prepared by treating this sulphate with barium carbonate. melts at 199°, and is identical with the compound obtained by A and C. Combes (*Bull. Soc. Chim.*, [2], **7**, 791) from acetylacetone and carbamide.

The condensation products of acetylacetone with thiocarbamide are obtained in a similar way to those with carbamide.

Acetylacetonethiocarbamide, $CS<^{N:CMe}_{N:CMe}>CH_2$, crystallises in yellow needles, melts at 210°, and easily yields compounds with metallic salts. The *silver salt*, $C_6H_7N_2SAg,AgNO_3$, is obtained as a white precipitate on adding silver nitrate to the aqueous solution. The aqueous solution also gives a white precipitate with mercuric chloride, a yellow precipitate with platinic chloride, an orange colora-

tion and then a yellowish precipitate with ferric chloride, and a dirty white precipitate with copper acetate. The *hydrochloride*,

$$C_6H_8N_2S,HCl,$$

crystallises in slender, yellow needles, and volatilises when heated on platinum. When the aqueous solution is treated with nitric acid and silver nitrate, it yields a white, crystalline precipitate which is not silver chloride; when boiled with alcoholic ammonia and mercuric oxide, the sulphur is not eliminated. The aqueous solution rapidly absorbs bromine, and the sulphur is then oxidised to sulphate. The *sulphate* crystallises in slender needles.

Dithiourimidoacetylacetone, $CH_2(CMe:N\cdot CS\cdot NH_2)_2$, was not obtained in the free state. The *hydrochloride* crystallises in yellow scales, melts at 219°, and immediately blackens. The aqueous solution gives a white precipitate with silver nitrate, which dissolves in ammonia with a dark brown coloration. The *sulphate* crystallises in four-sided tablets.

Urimidobenzoylacetone, $COPh\cdot CH_2\cdot CMe:N\cdot CO\cdot NH_2$, is obtained by adding concentrated hydrochloric acid to an alcoholic solution of benzoylacetone and carbamide. It forms small scales, melts at 191°, and, when treated with hydrochloric acid and then with ammonia, is converted into benzoylacetonecarbamide.

Benzoylacetonecarbamide, $CO{<}^{N\cdot CMe}_{N\cdot CPh}{>}CH_2$, is obtained either by heating benzoylacetone with carbamide or by treating an alcoholic solution of benzoylacetone and carbamide with hydrochloric acid. The first method does not give good results, and benzoylacetonamine, biuret, and cyanuric acid are formed. It melts at 228°. The *hydrochloride* sometimes separates out in yellow, rhombic plates. With platinic chloride and hydrochloric acid, it yields the salt

$$2C_{11}H_{10}N_2O,H_2PtCl_6,$$
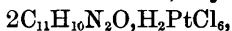
which crystallises in yellow rosettes. When heated with concentrated hydrochloric acid in a sealed tube at 160°, it remains unaltered.

Benzoylacetoneguanidine is obtained by heating a mixture of benzoyl-acetone and guanidine carbonate. It crystallises in small, sandy aggregates, melts at 173°, and easily yields salts with acids and metallic salts. The *platinochloride* crystallises in small, yellow needles. The solution in hydrochloric acid gives a white precipitate with mercuric chloride, and a soluble precipitate with ferric chloride. The solution in dilute nitric acid gives a crystalline precipitate with silver nitrate. It yields *two sulphates*, crystallising in white nodules and microscopic needles. The hydrochloride and nitrate crystallise in slender needles, the chromate in yellow needles. The *acetyl compound* crystallises in nodules, and melts at 146°. When it is dissolved in acetic acid, treated with nitrous acid, and the mixture poured into water and heated, it yields a brown, crystalline powder which melts at 205°.

The author was unable to obtain a condensation product from phenacetylacetone and carbamide or thiocarbamide.

Phenacetylacetoneguanidine, $NH\cdot C{<}^{N:C(CH_2Ph)}_{N \underset{=\!=}{\quad} CMe}{>}CH_2 + \frac{1}{2}H_2O$, is

obtained by heating phenacetylacetone with guanidine at 115—120°. It crystallises in needles, and melts at 108°. With platinic chloride and hydrochloric acid, it gives a yellow, crystalline precipitate.

<div align="right">E. C. R.</div>

Cuprammonium Double Salts. By T. W. RICHARDS and H. G. SHAW (*Amer. Chem. J.*, **15**, 642—653; compare Abstr., 1892, 953). —*Cuprammonium acetobromide*, $Cu(NH_3)_2Br\cdot C_2H_3O_2$, is formed by treating cupric bromide with alcoholic ammonia, and dissolving the cuprammonium bromide thus formed in alcoholic acetic acid. It forms fairly permanent, deep blue, apparently monoclinic crystals, and has the sp. gr. 2·134.

Ammoniocuprammonium acetochloride, $Cu(NH_3)_3Cl\cdot C_2H_3O_2 + H_2O$, is prepared by mixing concentrated solutions of copper chloride, acetic acid, and ammonia with alcohol. It forms brilliant, blue crystals of a pearly lustre, and loses ammonia and water slowly on exposure to the air.

Complex cuprammonium acetochloride,

$$[Cu(NH_3)_2ClC_2H_3O_2]_2,3NH_4\cdot C_2H_3O_2 + 7H_2O,$$
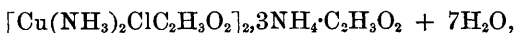
is formed when cupric chloride is treated with a large excess of concentrated ammonia, the excess cautiously neutralised with glacial acetic acid, and the whole treated with alcohol and allowed to evaporate. It forms brilliant, blue crystals of a violet tinge, and although soluble in a small quantity of water, it is decomposed by larger quantities. It decomposes when exposed to the air, losing water and ammonium acetate.

Cuprammonium formobromide, $Cu(NH_3)_2Br\cdot CHO_2$, is prepared similarly to the acetic compound.

Cupric ammonic acetochloride, $CuCl_2,2NH_4\cdot C_2H_3O_2$, occurs as a bye-product from some of the above preparations. It forms bright green, almost cubical crystals.

Tetrammoniotricuprammonium bromide, $3Cu(NH_3)_2Br_2,4NH_3$, is formed when strong hydrochloric acid is cautiously added to a solution of cupric bromide in the minimum quantity of alcoholic ammonia. It forms deep indigo crystals, and loses ammonia when moist, but is more stable when dry. It is converted by heat (160°) into an olive-green substance, $Cu(NH_3)_2Br_2$ (Abstr., 1891, 399), which still retains the original crystalline form. Rammelsberg's green, crystalline substance, $CuBr_2,5NH_3$, may have consisted of superficially decomposed crystals of the blue substance.

<div align="right">JN. W.</div>

Syntheses by means of Zinc Chloride. By I. KONDAKOFF (*J. pr. Chem.*, [2], **48**, 467—486; compare Abstr., 1893, i, 382).—The compounds of zinc chloride with olefine hydrocarbons have been dealt with (*loc. cit.*). The tertiary alkyl salts may be synthesised from olefines and organic acids in the presence of zinc chloride by keeping the three substances together at 20°; the ethereal salt is subsequently separated by decomposing the zinc chloride compound with water.

In this way tertiary amylic acetate has been prepared ; also *tertiary amylic formate*, a colourless liquid which boils at 112—113° (759 mm.), and has a sp. gr. of 0·9086 at 0°, and an odour of amylic

acetate; *tertiary amylic propionate*, which boils at 142—143·5° (757·3 mm.), and has a sp. gr. of 0·8769 at 0°; *tertiary amylic butyrate*, which boils at 164° (757·3 mm.), and has a sp. gr. of 0·8766 at 0°; *tertiary amylic isobutyrate*, which boils at 153—155° (762 mm.), and has a sp. gr. of 0·8706 at 0°; *tertiary amylic isovalerate*, which boils at 173—174° (762·3 mm.), and has a sp. gr. of 0·8729 at 0°; tertiary butylic acetate (b. p. 51°); and tertiary hexylic acetate (b. p. 143° at 757 mm.).   A. G. B.

Action of Ethylic Bromopropionate on Sodium Nitrite.

By G. LEPERCQ (*Bull. Soc. Chim.*, [3], **9**, 630—632).—When a mixture of ethylic bromopropionate, absolute alcohol, and sodium nitrite is heated gently on the water bath, it disengages carbonic anhydride, nitrogen, nitric oxide, and ethylic nitrite, and from the solution, a substance, $C_5H_9NO_3$, can be obtained in light, colourless needles of satiny lustre. It is identified with Meyer and Züblin's ethylic nitroso-propionate by the properties of its easily-formed silver salt; its boiling point (213°), however, differs from that (233°) given for the nitrosopropionate. It yields a granular solid nitrosopropionic acid. It is readily oxidised by potassium permanganate, but without the production of ethylnitrolic acid, although a nitrolic acid is obtained with nitrous acid in the ordinary way.   W. T.

Transformation Products of Normal α-Amidovaleric acid.

By A. MENOZZI and A. PANTOLI (*Gazzetta*, **23**, ii, 209—214).—The *iodide* of potassium α-trimethylamidovalerate, $COOK \cdot C_4H_8 \cdot NMe_3I$, is obtained by heating normal α-amidovaleric acid with methylic iodide in presence of potash. It is very hygroscopic, is soluble in water or alcohol, and crystallises in long, white needles. On adding a solution of iodine in hydriodic acid to its aqueous solution, a *periodide* of the base separates; this is ultimately obtained in well-developed crystals, having a metallic green lustre. When the periodide is suspended in water, and treated with hydrogen sulphide, *α-trimethylamidovaleric acid iodide* is obtained; this separates from dilute hydriodic acid in monosymmetric crystals containing $2H_2O$, $a : b : c = 1·4852 : 1 : 1·2459$; $\beta = 80° 33'$. It melts at 181—182°, is stable in the air, and soluble in water or alcohol. On crystallising it from alcohol, an *iodide* of the composition $(COOH \cdot C_4H_8 \cdot NMe_3)_2I$ is obtained, crystallising in cubes.

On treating the iodide melting at 181—182° with silver chloride, *α-trimethylamidovaleric acid chloride*, $COOH \cdot C_4H_8 \cdot NMe_3Cl$, is obtained; it forms small, transparent prisms, and is soluble in water or alcohol. With platinic chloride, it yields a *methylic platinochloride* of the composition $(COOH \cdot C_4H_8 \cdot NMe_2)_2, Me_2PtCl_6, 2H_2O$; this forms yellow prisms which lose water at 100° and melt at 219°. The *methylic aurochloride*, $COOH \cdot C_4H_8 \cdot NMe_2, MeAuCl_4$, is obtained in anhydrous, yellow laminæ which melt at 160°.

On treating the iodide of the potassium salt described above with moist silver oxide in aqueous solution, silver iodide is deposited: this is filtered off, the alkaline solution concentrated, and the residue

heated at 120°. Trimethylamine is evolved, and, on treating the product with dilute sulphuric acid, *propylideneacetic acid*,

$$CH_2Me\cdot CH\!:\!CH\cdot COOH,$$
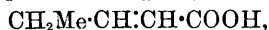
is liberated; this is a colourless oil which boils at 194—195°, and remains liquid at —16°; it has an odour resembling that of α-crotonic acid. It is heavier than water at 0°. but lighter at 15°. The propylideneacetic acid prepared by Ott (Abstr., 1891, 1453) and others does not coincide in properties with the authors' product; several of the salts of the acid are described. During the preparation of this acid, a small quantity of normal α-hydroxyvaleric acid is obtained.

W. J. P.

Composition of Rape Oil. By G. PONZIO (*J. pr. Chem.*, [2], **48**, 487—488).—Reimer and Will (Abstr., 1887, 1030) state that rape oil contains the glycerides of erucic and rapic acids, in about equal proportions, and a little behenic acid. The author shows that their behenic acid is arachidic acid, which the oil contains to the extent of about 4 per cent. Arachidamide melts at 108° (compare Schweizer, Abstr., 1885, 508). A. G. B.

A Nitrogenous Acid in Beet Juice. By E. O. v. LIPPMANN (*Ber.*, **26**, 3061—3063).—A yellow, crystalline deposit was obtained while working up the juice of beets which had been frozen and thawed. The author has isolated from this deposit an acid which he believes to be citrazinic acid, $C_6H_5NO_4$. It is a yellow, crystalline powder, scarcely soluble in boiling water, decomposes at 300° with an odour resembling that of burning hair, and is soluble in alkalis and alkali carbonates. E. C. R.

Oxidation of Diallyloxalic acid with Potassium Permanganate. By S. FOKYN (*J. pr. Chem.*, **48**, 522—533).—Bulitsch has shown that a tetrahydroxyoctolactone is obtained by oxidising diallyloxalic acid with nitric acid. On the other hand, Schutzky could not obtain this lactone by oxidising with permanganate; the author, however, finds that by careful oxidation with this agent, under conditions detailed in the original paper, the lactone is obtained together with a lactonic acid.

The *lactonic acid*, $OH\cdot CH_2\cdot CH{<}^{CH_2-}_{O\cdot CO}{>}C(OH)\cdot CH_2\cdot COOH$, is a yellowish syrup, and has a sour taste. The *calcium* salt, $C_7H_{10}O_7Ca$, and the *barium salts*, $C_7H_{10}O_7Ba$ and $(C_7H_9O_6)_2Ba$, are described.

Tetrahydroxyoctolactone,

$$OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot C(OH){<}^{CH_2}_{COO}{>}CH\cdot CH_2\cdot OH,$$
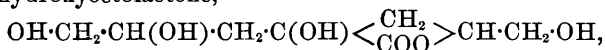
is a syrup and has a sweet taste. The *calcium salt*, $(C_8H_{15}O_7)_2Ca + 2H_2O$, and *barium salt*, $(C_8H_{15}O_7)_2Ba$, a yellowish, glassy, hygroscopic mass, melting at 84°, were obtained. This lactone differs from the compound obtained by the oxidation of diallyloxalic acid with nitric acid as shown by a comparison of the salts   The calcium and barium

salts, $(C_8H_{15}O_7)Me''$, obtained by Bulitsch are glassy, whereas the calcium salt obtained by the author is crystalline. These two salts, moreover, cannot be converted into salts of the composition $(C_8H_{13}O_6)_2Me''$; the author's lactone does not yield basic salts $C_8H_{12}O_6Me''$ and $(C_8H_{13}O_7)_2Me''_3$, even when boiled with the alkaline earths. Finally, Bulitsch's lactone yields an insoluble lead salt, whereas the lead salt of the above lactone is soluble. E. C. R.

Ethereal Salts of Oxalacetic acid. By W. WISLICENUS and A. GROSSMANN (*Annalen,* **277**, 375—383).—*Methylic oxalacetate,* $COOMe \cdot CO \cdot CH_2 \cdot COOMe$, is prepared by adding methylic oxalate together with ether to solid sodium methoxide, and subsequently heating the mixture with methylic acetate on the water bath; the *sodium* derivative thus obtained is decomposed by dilute sulphuric acid. The methylic salt crystallises in colourless, lustrous needles, melts at 74—76°, and boils at 137° under 39 mm. pressure; the alcoholic solution gives a red colour with ferric chloride. The *copper* derivative, $(C_6H_7O_5)_2Cu$, forms small, green needles, and melts at 214—215° with decomposition. The phenylhydrazone, already described by Buchner (Abstr., 1890, 156), yields *methylic phenylpyr-azolonecarboxylate,* $COOMe \cdot C \underset{CH_2 \cdot CO}{\overset{N-NPh}{<\!\!|}}$, when heated above its melting point; this forms white crystals, and melts at 197°.

Amylic oxalacetate, $COO(C_5H_{11}) \cdot CO \cdot CH_2 \cdot COO \cdot C_5H_{11}$, is obtained by adding amylic oxalate and ether to solid sodium ethoxide, and subsequently amylic acetate, and decomposing the sodium compound with dilute acid. It is an oil having an unpleasant odour, boils at 167° under a pressure of 23 mm., and the alcoholic solution gives a deep red coloration with ferric chloride; it yields an oily *phenyl-hydrazone,* which condenses to *amylic phenylpyrazolonecarboxylate* when heated at 190°. The *copper* derivative melts at 83—85°.

Methylic ethylic oxalacetate, $COOMe \cdot CH_2 \cdot CO \cdot COOEt$, prepared from ethylic oxalate and methylic acetate as in the above cases, is a colourless oil boiling at 130° (22 mm.), and at 124° (16 mm.); the *copper* derivative melts at 134—135°. When the *phenylhydrazone* is heated, it is converted into *ethylic phenylpyrazolonecarboxylate,* $COOEt \cdot C \underset{CH_2 \cdot CO}{\overset{N-NPh}{<\!\!|}}$, melting at 180—182°. A. R. L.

Preparation of Amides. By A. VERLEY (*Bull. Soc. Chim.,* [3], **9**, 690—692).—Distillation of dry potassium or sodium salts of the organic acids with ammonium (or a replaced ammonium) chloride gives a better yield of the corresponding amides than distillation of the ammonium salts directly, and the product is readily purified. In this way 80 per cent. of the theoretical yield of acetamide has been obtained.

Methylamine hydrochloride distilled with potassium acetate and a little acetic acid gives 88 per cent. of the theoretical yield of methyl-acetamide. Similarly, a yield of 91 per cent. of dimethylacetamide is obtained. With formamide, the yield is 78 per cent. Succinimide

requires the ammonium chloride and potassium succinate to be intimately mixed. The yield of product, purified by recrystallisation after treatment with animal black, is 87 per cent. of the theoretical.

Dimethylformamide.—This substance is prepared exactly like dimethylacetamide. It is a liquid of a feeble but not disagreeable odour, boiling without decomposition at 155°; sp. gr. 0·968 at 20°.

W. T.

Formation of Dithïenyl Derivatives from Thiophen. By A. Töhl and O. Eberhard (*Ber.*, **26**, 2945—2947).

—When sulphuryl chloride is mixed with thiophen and a small quantity of aluminium chloride added, a violent action takes place, sulphurous anhydride and hydrogen chloride being evolved. The residue contains small quantities of chlorothiophen, but consists chiefly of a mixture of trichlorodithïenyl and dichlorodithïenyl. *Trichlorodithïenyl*, $C_8S_2H_3Cl_3$, forms short needles, and melts at 103°; it is converted by the action of bromine into *trichlorotribromodithïenyl*, $C_8S_2Cl_3Br_3$, which crystallises in long, pale yellowish needles, and melts at 214—215°. *Dichlorodithïenyl*, $C_8S_2H_4Cl_2$, forms thin, yellowish plates, melts at 109—110°, and, on treatment with bromine, yields *dichlorotetrabromodithïenyl*, $C_8S_2Cl_2Br_4$, which crystallises in reddish needles, and melts at 221—222°.

H. G. C.

Action of Sulphuric acid on Chlorothiophen. By A. Töhl and O. Eberhard (*Ber.*, **26**, 2947—2949).

—The presence of small quantities of chlorothiophen in the product of the action of sulphuryl chloride on thiophen in presence of aluminium chloride (see preceding abstract) leads to the supposition that this is the first product of the action, and that it undergoes condensation to dithïenyl derivatives in presence of sulphuryl chloride. The authors have therefore endeavoured to bring about the same condensation by treating chlorothiophen with concentrated sulphuric acid. The α-chlorothiophen is obtained in much larger quantity from sulphuryl chloride and thiophen if the mixture is diluted with ether, and may be readily prepared in this manner. When treated with sulphuric acid, it is converted chiefly into *chlorothiophensulphonic acid* and *chlorodithïenyl*, $C_8S_2H_5Cl$, but the latter could not be obtained quite pure; with bromine this yields *chloropentabromodithïenyl*, $C_8S_2ClBr_5$, which crystallises in long, white needles, and melts at 238—240°. The *barium* salt of chlorothiophensulphonic acid, $(C_4SH_2Cl·SO_3)_2Ba + 2H_2O$, crystallises from alcohol in small druses of white needles.

H. G. C.

New Method of preparing Iodochlorides. By A. Töhl (*Ber.*, **26**, 2949—2950).

—A very good yield of the iodochlorides may be obtained by treating the iodo-derivative with sulphuryl chloride in ethereal solution, the presence of a little water being necessary to start the reaction. Satisfactory results have been obtained by this method with iodobenzene, pariodotoluene, 1 : 3 : 4-iodometaxylene, and iodomesitylene.

H. G. C.

Electrolytic Reduction of Nitrobenzene. By C. Haeussermann (*Chem. Zeit.*, **17**, 129 and 209).—This paper was published prior to those of Gattermann and Koppert (Abstr., 1893, i, 567; this vol., i, 72). The reduction of nitrobenzene in alkaline solution is carried out as follows:—Nitrobenzene (25 grams) dissolved in alcohol (350 c.c.) and mixed with a solution of sodium hydroxide (40 grams) in water (50 c.c.) is introduced into a porous cell which contains the cathode (iron or platinum, according to the nature of the solution) ; the porous cell stands in an outer vessel containing a platinum or carbon anode and filled with dilute sodium hydroxide. A current of 6—8 ampères at a potential of 6 volts is used. The precipitation of hydrazobenzene at the cathode soon commences, and at the end of 10 hours benzidine is obtained. Orthonitrotoluene yields the corresponding compounds, but in smaller quantity than nitrobenzene. If the reduction is conducted in acid solution, the porous cell is charged with nitrobenzene (25 grams), sulphuric acid (30 grams), water (100 c.c.), and alcohol (350 c.c.). The current used is 5 *ampères* at a potential of 4·5 volts. Benzidine sulphate soon commences to separate at the cathode, and on adding water to the filtrate azoxybenzene is precipitated. When the solutions are previously heated to 60°, traces of aniline are also formed, whereas the greater portion of the nitrobenzene remains unaltered, so that the electrolytic production of aniline seems impracticable ; the same may be said of that of ortho- and para-toluidine. When, however, a solution of metanitrobenzenesulphonic acid in dilute sulphuric acid is submitted to a current of 3 ampères at a potential of 4 volts, metanilinesulphonic acid is obtained.   A. R. L.

Action of Carbonyl Chloride on Picramic acid. By F. Rudolf (*J. pr. Chem.*, [2], **48**, 425—446).—Finely powdered picramic acid, m. p. 168—169° (uncorr.), was heated at 130—140° for 4—5 hours with a 15 per cent. solution of carbonyl chloride in chloroform, in a sealed tube. The solid product of the reaction was washed with chloroform and crystallised from water.

The *hydroxydinitrophenyl isocyanate,*

$$OH \cdot C_6H_2(NO_2)_2 \cdot N \vdots CO \ [OH : N : (NO_2)_2 = 1 : 2 : 4 : 6],$$
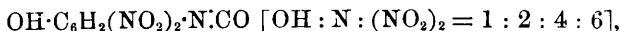
thus obtained, crystallises in small, nearly white, obliquely truncated prisms, and in long needles. It melts at 222—223° (uncorr.), and dissolves very sparingly in cold water, more freely in hot water, ether, acetone, concentrated sulphuric acid, and glacial acetic acid, sparingly in benzene, and not at all in chloroform. Its solutions are acid ; when heated with water for some hours, it is hydrolysed into picramic acid and carbonic anhydride. The *sodium, potassium,* and *silver* derivatives, corresponding with the formula

$$OM \cdot C_6H_2(NO_2)_2 \cdot N \vdots CO,$$

were prepared.

When the isocyanate is heated with ammonia in aqueous or alcoholic solution, the *ammonium* derivative of *carbamidodinitrophenol,* $NH_4 \cdot O \cdot C_6H_2(NO_2)_2 \cdot NH \cdot CO \cdot NH_2$, is obtained in the form of small, thick,

red prisms. The carbamidodinitrophenol, liberated by acidifying the ammonium salt, is identical with Griess' uramidodinitrophenylic acid (*J. pr. Chem.*, [2], **5**, 1); by hydrolysis, it is converted into the original isocyanate and ammonia.

With aniline, the isocyanate forms *phenylcarbamidodinitrophenol*, $OH \cdot C_6H_2(NO_2)_2 \cdot NH \cdot CO \cdot NHPh$, which crystallises in microscopic, red prisms, and decomposes at 200°. With phenylhydrazine, *phenylhydrazine carbamidodinitrophenol phenylhydrazide*,

$$N_2H_3Ph, OH \cdot C_6H_2(NO_2)_2 \cdot NH \cdot CO \cdot N_2H_2Ph,$$

is produced; it crystallises in orange needles, and decomposes at 130°; when heated with solvents, it loses phenylhydrazine, becoming *phenylhydrazinecarbamidodinitrophenol*, $OH \cdot C_6H_2(NO_2)_2 \cdot NH \cdot CO \cdot N_2H_2Ph$, which crystallises in microscopic needles, and melts with decomposition at 202—203°.

By heating the isocyanate with alcohol, *ethylic hydroxydinitrophenylcarbamate* is obtained; this crystallises in yellow needles, melts at 153°, and dissolves in the usual organic solvents except light petroleum. When heated with hydrochloric acid, it yields ethylic chloride, carbonic anhydride, and picramic acid hydrochloride. The *ammonium*, *potassium*, and *silver* derivatives are described. The corresponding *methylic salt*, analogously prepared, crystallises in yellow needles, and melts at 179° (uncorr.). A. G. B.

Action of Sodium on γ-Bromopropylphenyl Ether. By W. SALONINA (*Ber.*, **26**, 2987—2988).

The author describes the preparation of hexamethylene derivatives from γ-bromopropylphenyl ether. The latter substance, when heated with sodium, yields, in addition to sodium phenoxide, a small amount of hexamethyleneglycoldiphenyl ether, $OPh \cdot CH_2 \cdot [CH_2]_4 \cdot CH_2 \cdot OPh$, which crystallises from alcohol in long needles, melts at 83°, and is only slightly soluble in cold alcohol. When this ether is heated with concentrated hydrobromic acid at 150°, it is converted into hexamethylene dibromide, $CH_2Br[CH_2]_4 \cdot CH_2Br$, which boils at 240—247° without decomposition. Hydriodic acid at 110° converts the diphenyl ether into the corresponding diiodide, $CH_2I \cdot [CH_2]_4 \cdot CH_2I$, which is an almost colourless liquid, decomposes on distillation, and solidifies, on cooling, to a mass which melts at −7°. The author is continuing his investigations. A. H.

Compounds of Picric acid with Phenols and Ketones. By R. v. GOEDIKE (*Ber.*, **26**, 3042—3046).

The compounds are obtained by adding a hot saturated solution of picric acid in 50 per cent. alcohol to a similar solution of the phenol. A small excess of phenol is used, to prevent the compound being contaminated with picric acid. The picrates are somewhat stable, but decompose when heated at 100° or in a desiccator over sulphuric acid. They are also decomposed by boiling with ammonia or soda.

Phenol picrate, $C_6H_5 \cdot OH, 2C_6H_3N_3O_7$, crystallises in bright yellow needles, and melts at 53°.

Orthocresol picrate, $2C_7H_7 \cdot OH, 3C_6H_3N_3O_7$, crystallises in orange

k 2

needles, and melts at 88°. Neither metacresol nor paracresol combines with picric acid.

Ortho-xylenol picrate, $5C_8H_9\cdot OH,4C_6H_3N_3O_7$, forms orange crystals, and melts at 82°. Paraxylenol also yields a picrate; metaxylenol does not.

Of the dihydroxybenzenes, only pyrocatechol combines with picric acid. The *picrate*, $C_6H_4(OH)_2,C_6H_3N_3O_7$, crystallises in orange needles, and melts at 122°.

Guaiacol picrate crystallises in beautiful, orange needles, and melts at 86°. *Creosol picrate* crystallises in yellow needles, and melts at 96°. *Ethylguaiacol picrate* crystallises in orange needles, and melts at 90°. *Propylguaiacol picrate* crystallises in red needles, and melts at 59°.

Pyrogallol and phloroglucinol do not yield picrates. *Dimethylpyrogallol picrate* crystallises in yellow needles, and melts at 53°.

Orthochlorophenol picrate, $C_6H_4Cl\cdot OH,C_6H_3N_3O_7$, crystallises in bright yellow needles, and melts at 81—82°.

Acetophenone picrate, $COMePh.C_6H_3N_3O_7$, forms greenish yellow, quadratic crystals, and melts at 53°.

Gallacetophenone picrate crystallises in orange needles, and melts at 133°.

The author draws attention to the fact that, as a rule, it is only the ortho-compounds which are able to form picrates.   E. C. R.

Essence of Tarragon and its Conversion into Anethoïl. By E. GRIMAUX (*Compt. rend.*, **117**, 1089—1092).—When essence of tarragon is subjected to fractional distillation, about 60 per cent. boils between 210° and 215°, and after four distillations this product boils between 210·5° and 212° under a pressure of 747·4 mm. Neither the crude essence nor the purified product contains any anethoïl.

Estragoïl $C_{10}H_{12}O_2$, the chief constituent of essence of tarragon, boils at 215—216° (corr.); sp. gr. at 15° = 0·9325; index of refraction for D = 1·523. Its boiling point is 16—17° below that of anethoïl.

Estragoïl is easily converted into anethoïl by heating it on a water bath for about 24 hours with three or four times its weight of concentrated alcoholic potash, and the product is identical with the anethoïl obtained from the oil of aniseed.

It would seem that estragoïl and anethoïl differ in the isomerism of the group C_3H_5, the constitution of the former being

$$OMe\cdot C_6H_4\cdot CH_2\cdot CH\!:\!CH_2,$$
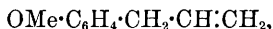
and of the latter $OMe\cdot C_6H_4\cdot CH\!:\!CHMe$, the difference being the same as that which exists between eugenol and isoeugenol, safrole and isosafrole. The difference between the boiling points of the two isomerides is practically the same in all three cases.

The methyl derivative of the chavicol obtained by Eykmann from the oil of the betel nut boils at 226°, and is probably a stereoisomeride of anethoïl, and not a propenylic derivative like estragoïl.

C. H. B.

Condensation Products of Monobasic acids with Resorcinol. By G. COHN (*J. pr. Chem.*, [2], **48**, 384—410; compare Abstr., 1893, i, 719).—The following conclusions are drawn:—(1) Monobasic

acids condense with resorcinol, under certain conditions, to form fluoresceïns. (2) The character of these colouring matters is independent of the nature of the acid, for they are all similar in colour, fluorescence, spectrum, solubility, and in the nature of their derivatives. (3) All give similar tetrabromo-substitution products, eosins containing the bromine in the resorcinol nucleus. (4) The influence of the acid is exhibited in the facts that (*a*) aliphatic fluoresceïns show a smaller affinity for animal fibres than do aromatic fluoresceïns ; and (*b*) the more complex acids yield more highly halogenised, redder derivatives. (5) Benzoic acid and benzotrichloride, with resorcinol and zinc chloride, yield the same colouring matter, whilst benzaldehyde gives a product which differs from the benzeïns.

<div align="right">A. G. B.</div>

Reaction of Sodium Alkyloxides with Tribromotrinitrobenzene. By C. L. JACKSON and W. H. WARREN (*Amer. Chem. J.*, **15**, 607—642; compare Abstr., 1891, 1024).—With sodium ethoxide, tribromotrinitrobenzene yields diethyltribromonitroresorcinol, triethyltrinitrophloroglucinol, and the products of hydrolysis of the latter.

Diethyltribromonitroresorcinol is converted by boiling alcoholic sodium hydroxide, with elimination of bromine, into *diethylbromonitroresorcinol* $NO_2 \cdot C_6H_2Br \cdot (OEt)_2$, a substance crystallising in long, silky, white needles, and melting at 115°.

Triethyltrinitrophloroglucinol, $C_6(NO_2)_3(OEt)_3$ crystallises in long, slender plates, turns brown on exposure to the air, and melts at 119—120°. It is hydrolysed by alcoholic sodium hydroxide into *diethyltrinitrophloroglucinol*, $OH \cdot C_6(NO_2)_3(OEt)_2$, and *trinitrophloroglucinol* with $1H_2O$. The former crystallises in straw-coloured needles or prisms, and melts at 89°. It decomposes alkaline carbonates; the sodium salt crystallises in fine, orange-red needles. The latter crystallises in yellow, hexagonal prisms, and, when free from water, melts at 167°. The low melting point (158°) found by Benedikt (*Ber.*, **11**, 1376) was probably due to imperfect dehydration. The two substances are formed in the preparation of the triethyl compound if moisture is not excluded, the hydrolysis being effected by sodium hydroxide formed by the action of moisture on the sodium ethoxide. The influence of benzene on the relative proportion of the phloroglucinol and resorcinol compounds was investigated, and it was found that less nitrous acid (33·5 per cent. of the theoretical) was evolved, and therefore less resorcinol compound formed, when benzene was present than when alcohol alone was used (45·9 per cent.). In the presence of ethylic acetate, the principal product was dinitrobromophenetoïl, m. p. 147°, the formation of which was probably due to the hydrolysis of the resorcinol compounds, since when the solvents were previously dried the yield was much less.

By the action of a solution of sodium methoxide in methylic alcohol on tribromotrinitrobenzene, dimethyltribromonitroresorcinol (*loc. cit.*) is formed together with *dimethyltrinitrophloroglucinol*, crystallising in yellowish needles, and melting at 77—78°. The alkali salts are yellow.

Sodium propoxide in the presence of alcohol and benzene yields

tripropyltrinitrophloroglucinol, a substance crystallising in yellow prisms, and melting at 109—110°. The corresponding *isopropyl compound* crystallises in colourless prisms, and becomes orange on exposure to the air; it melts at 130°. Sodium isobutoxide and isoamyloxide also react with tribromotrinitrobenzene, but the products were not examined. Nitrite as well as bromide was formed in all the above cases; the relative amount of nitrite tended to diminish as the molecular weight increased.

Sodium benzyloxide in benzylic alcohol solution (prepared by dissolving sodium in benzylic alcohol) yields, with a benzene solution of tribromotrinitrobenzene, *tribenzyltrinitrophloroglucinol* and trinitrophloroglucinol. The former substance crystallises in white needles and is discoloured by the air; it melts at 171°. A small quantity of benzylic bromide is also formed. Since this substance is without action on the sodium salt of trinitrophloroglucinol, its presence may be due to the direct action of the sodium benzyloxide on the trinitrotribromobenzene.

Triphenyltrinitrophloroglucinol, $C_6(NO_2)_3(OPh)_3$, is converted by alcoholic sodium ethoxide into the corresponding ethyl compound, with elimination of phenol.   Jn. W.

Some Peculiar Cases of Isomerism. By R. FABINYI (*Zeit. physikal. Chem.*, **12**, 564—582).

—When asarone is dissolved in absolute alcohol, and amylic nitrite and then alcoholic hydrogen chloride are added to the cooled solution, green prisms (m. p. 159·4°) of asarylaldoxime hydrochloride are obtained. If, however, the alcoholic hydrogen chloride be added first, and then the amylic nitrite, red prisms are formed which melt at 161·6°. These, on analysis, were found by the author to give numbers also corresponding with asarylaldoxime hydrochloride, and were thus isomeric with the green prisms. The free aldoximes from these salts are both anti-aldoximes; they differ very slightly from each other, and give acetyl compounds which are still more similar, one and the same aldoxime being regenerated from the two acetyl derivatives. The hydrochlorides, on repeated recrystallisation from glacial acetic acid, approximate gradually to each other in colour, melting point, and solubility, the final substance obtained from both being golden yellow, and melting at 155·5°. The hydrochloride of the aldoxime prepared directly from asarylaldehyde crystallises in golden yellow needles which melt at 155·4°.

Several other examples of similar cases of isomerism are alluded to.   J. W.

New Formation of Secondary Aromatic Amines. By V. MERZ and S. PASCHKOWEZKY (*J. pr. Chem*, [2], **48**, 454—466).

—The method consists in heating halogen benzene hydrocarbons with primary amines and a strong inorganic base. In this way, phenylparatolylamine is obtained from bromo-, chloro-, and iodo-benzene respectively, and paratoluidine; also from parabromo- and pariodotoluene respectively, and aniline. Phenylorthotolylamine is obtained from bromobenzene and orthotoluidine; diphenylamine from bromobenzene and excess of aniline; diparatolylamine from parabromo-

toluene and paratoluidine ; and aniline from bromobenzene and ammonia.
A. G. B.

Isomerism in the Azo-Series. By J. T. HEWITT (*Ber.*, **26**, 2975—2978).—*Orthochlorobenzeneazophenol*, $C_6H_4Cl \cdot N_2 \cdot C_6H_4 \cdot OH$, prepared by treating a mixture of orthochloraniline nitrate and phenol with potassium nitrite, is precipitated from alcoholic solution by the addition of water in fine, yellow needles melting at 85°. It is very readily soluble in the usual organic solvents, but almost insoluble in water, and is precipitated from its solution in alkalis by carbonic anhydride. When heated for an hour at 80°, it is converted into a light red substance of the same composition, melting at 96°. This modification behaves in the same way towards solvents as the yellow form, but the latter is precipitated by acids from its solutions in alkalis, and by water from alcoholic solution. This behaviour might be accounted for either by tautomerism as expressed in the formulæ $C_6H_4Cl \cdot N{:}N \cdot C_6H_4 \cdot OH$ and $C_6H_4Cl \cdot NH \cdot N{:}C_6H_4{:}O$, or by geometrical isomerism, $\begin{matrix} C_6H_4Cl \cdot N \\ \| \\ OH \cdot C_6H_4N \end{matrix}$ and $\begin{matrix} C_6H_4Cl \cdot N \\ \| \\ N \cdot C_6H_4 \cdot OH \end{matrix}$. Both the modifications when treated with acetic anhydride yield the same *acetate*, which crystallises in fine yellow needles, and melts at 100°. It is insoluble in water, readily soluble in alcohol, &c. The *benzoate* crystallises from hot alcohol in yellow plates, melting at 131°.

Metachlorobenzeneazophenol crystallises from dilute alcohol in splendid, brownish-violet needles, which, after heating at 80°, become pale yellow, and then melt at 135°. The *acetate* separates from dilute alcohol in yellowish-red plates melting at 92°. The *benzoate* forms yellow scales, and melts at 118°.

Parachlorobenzeneazophenol, which was previously known, does not yield an isomeric form when heated. Its *acetate* crystallises from alcohol in hair-like, yellow needles, and melts at 160°. The *benzoate* forms small, yellowish-red plates melting at 154°.
A. H.

Diazosulphides. By P. JACOBSON (*Annalen*, **277**, 209—218).—An introductory paper (see following abstracts and p. 137). The orthodiazosulphides, unlike the orthodiazooxides, are colourless compounds resembling in this respect the azimides obtained by the action of nitrous acid on the orthodiamines. They generally crystallise well, have a characteristic, sweetish odour, and are very feebly basic. The first representative of the class, chlorophenylene diazosulphide, was obtained by Beilstein and Kurbatow (*Annalen*, **179**, 82). Bernthsen (Abstr., 1889, 775) described another member of the group, namely, diazothiodimethylaniline, whilst the simplest members were prepared by the author (Abstr., 1889, 135 and 772).
A. R. L.

Phenylene Diazosulphide and its Derivatives. By P. JACOBSON and H. JANSSEN (*Annalen*, 177, 218—231).—Phenylene diazosulphide, $C_6H_4{<}{{}^N_S}{>}N$ (Abstr., 1889, 135), is prepared by the action of nitrous acid on amidophenyl mercaptan. The compound melts at 35·5—36°,

when heated in a capillary tube, whilst by introducing a thermometer into a quantity of the fused substance the solidifying point (?) was found to be $34\cdot95°$; it boils at $129°$ (corr.) under a pressure of 10 mm., and at $188°$ (corr.) under a pressure of 150 mm. It is insoluble in dilute acids, but dissolves in concentrated hydrochloric acid, being reprecipitated on dilution with water; a molecular weight determination by the cryoscopic method established the above formula. A quantity of the compound ($0\cdot3—0\cdot5$ gram) dissolved in 5) per cent. alcohol and injected subcutaneously into a rabbit causes death in 48 hours; the toxic phenomena consist in the gradual paralysis of the central nervous system accompanied by a continuous lowering of the temperature. The *platinochloride*, $(C_6H_4N_2S)_2,H_2PtCl_6$, forms small, six-sided tablets; a crystalline additive *compound*, $C_6H_4N_2S,HgCl_2$, was also obtained. Phenylene diazosulphide remains unaltered when heated in sealed tubes with alcohol at $150—160°$, with 20 per cent. potash at $150°$, and with 27 per cent. sulphuric acid at $200°$, or when boiled with alcoholic ammoniacal silver solution. When boiled with tin and hydrochloric acid, orthoamidophenyl mercaptan is formed, whilst, if treated with oxidising agents, the greater portion remains unaltered, and the remainder appears to undergo complete combustion. When heated at $200—250°$ until gas ceases to be evolved, the residue consists of diphenylene bisulphide, $C_6H_4{<}{\genfrac{}{}{0pt}{}{S}{S}}{>}C_6H_4$.

Methylphenylenediazosulphine iodide, $\genfrac{}{}{0pt}{}{C_6H_4\cdot N}{SMeI-}{\gg}N$, is prepared by heating phenylene diazosulphide with an excess of methylic iodide in a sealed tube at $100°$; it crystallises from water in red needles. The *compound* $\genfrac{}{}{0pt}{}{C_6H_4\cdot N}{SEtI—}{\gg}N$ forms stout, red prisms.

Methylphenylenediazosulphine chloride, $\genfrac{}{}{0pt}{}{C_6H_4\cdot N}{SMeCl}{\gg}N$, is obtained by digesting a solution of the iodide with silver chloride; it crystallises in colourless, hydrated prisms. When concentrated solutions of ammonium picrate are added to those of the iodide, double decomposition ensues, and crystalline picrates are precipitated.

<div align="right">A. R. L.</div>

Homologues of Phenylene Diazosulphide. By P. JACOBSON and E. NEY (*Annalen*, **277**, 232—236).—The homologues of phenylene diazosulphide are prepared from the ethenyl compounds of the corresponding amidomercaptans (compare Abstr., 1889, 772); the latter being heated with alcoholic potash in sealed tubes at $180—190°$, and the resulting amidomercaptans treated with nitrous acid.

Toluylene diazosulphide, $C_6H_3Me{<}{\genfrac{}{}{0pt}{}{N}{S}}{\gg}N$ [Me : S : N $= 1:3:4$], crystallises in colourless tables, melts in a capillary tube at $42—43°$, and distils without decomposition under diminished pressure; the solidifying point (?) determined with a large quantity of the fused substance is $40\cdot9°$. On reduction with tin and hydrochloric acid,

it behaves in an analogous manner to phenylene diazosulphide, and, when heated at 200—220°, it yields *ditoluylene bisulphide*,

$$C_6H_3Me<^S_S>C_6H_3Me,$$
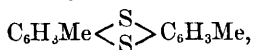
which crystallises in faintly yellowish needles, and melts at 116°; *methyltoluylenesulphine iodide* forms beautiful golden-yellow prisms.

Xylylene diazosulphide, $C_6H_2Me_2<^N_S\!\!\gg\!N$ [$Me_2 : N : S = 1 : 3 : 4 : 5$], crystallises in lustrous needles, and melts at 37°; *dixylylene bisulphide*, $C_6H_2Me_2<^S_S>C_6H_2Me_2$, prepared by heating it at 250°, melts at 118°. Xylylene diazosulphide shows little tendency to combine with methylic iodide, and, when heated in a sealed tube at 100° with it, only a very small quantity of a compound soluble in water is obtained.

Cumylene diazosulphide, $C_6HMe_3<^N_S\!\!\gg\!N$, crystallises in prisms, and melts at 85°; its odour is faint and not characteristic, and it loses its nitrogen at a higher temperature (270°) than the lower homologues, but a homogeneous substance could not be isolated from the residue.

A. R. L.

Substitution Derivatives of Phenylene Diazosulphide. By P. JACOBSON and A. KWAYSSER (*Annalen*, **277**, 237—256).—*Nitro-carbimidothiophenol*, $NO_2\!\cdot\!C_6H_3<^N_S\!\!\gg\!C\!\cdot\!OH$, is thus prepared. Phenyl-thiocarbimide is boiled for 18 hours with absolute alcohol, and the phenylthiourethane thus formed is oxidised with alkaline potassium ferricyanide (see Abstr., 1886, 876). The product, ethoxyphenyl-thiocarbimide, is then hydrolysed with hydrochloric acid, whereby carbimidothiophenol is obtained, which is dissolved in glacial acetic acid, and treated in the cold with nitric acid of sp. gr. 1·52. The nitro-derivative crystallises in stellate aggregates of light yellow needles, and melts at 252°. When an excess of soda is added to its solution in dilute soda, the *sodium* salt separates as a yellow, crystalline precipitate. The *ethylic* salt forms faintly yellow, silky needles, and melts at 205°.

Nitramidophenyl mercaptan, $NO_2\!\cdot\!C_6H_3(NH_2)\!\cdot\!SH$ [$NO_2 : NH_2 : SH = 5 : 2 : 3$] (Mylius, *Inaug. Diss.*, 1883), is obtained by heating nitro-carbimidothiophenol with aqueous ammonia of sp. gr. 0·95 in a sealed tube at 160—170°; it forms microscopic, pale yellow needles, melts at 83—84°, and is oxidised when exposed in the moist condition to the air, forming the bisulphide, $S_2[C_6H_3(NH_2)\!\cdot\!NO_2]_2$; this compound is, however, best prepared by oxidising the mercaptan with ferric chloride; it crystallises in lemon-yellow needles, and melts at 236—237°. When the mercaptan is digested with concentrated formic acid, the methenyl derivative, $NO_2\!\cdot\!C_6H_3<^N_S\!\!\gg\!CH$ (Mylius, (*loc. cit.*), melting at 176—177°, is produced.

Nitrophenylene diazosulphide, $NO_2\!\cdot\!C_6H_3<^N_S\!\!\gg\!N$, is obtained by the

action of nascent nitrous acid on the nitramidophenyl mercaptan; it crystallises in golden-yellow leaflets, melts at 136—137°, and, when reduced with ammonium sulphide, yields the corresponding *amido-phenylene diazosulphide*, which crystallises in long, colourless needles, and melts at 112°; when a solution of the base in hydrochloric acid is treated with sodium nitrite, a dark violet coloration is produced on the addition of α-naphthol, and a brownish-red coloration on the addition of resorcinol. Attempts to prepare the amidophenylene diazosulphide by the action of nitrous acid on diamidophenyl mercaptan were unsuccessful. The author found it impossible to prepare hydroxyphenylene diazosulphide from the amido-derivative by the diazo-reaction.

Nitrocarbimidothiophenol (see above), when reduced with stannous chloride and hydrochloric acid, yields the corresponding *amido-*compound, which crystallises in dull, colourless needles, melts at 222—223°, and forms a *picrate* melting at 242°.

Cyanocarbimidothiophenol, $CN \cdot C_6H_3 <^N_S> C \cdot OH$, obtained from the amido-compound, by Sandmeyer's method, forms pale yellow, microscopic needles, melts (not sharply) above 250°, and when fused with potash yields *carboxyamidothiophenol*, which was not isolated, but converted by treatment with nascent nitrous acid into carboxyphenylene diazosulphide, $COOH \cdot C_6H_3 <^N_S> N$; this was purified by means of the *methylic* salt (m. p. 150—151°). The free acid, obtained by the hydrolysis of the methylic salt with 10 per cent. potash, forms nodular, radiating aggregates of minute needles, melts at 138—139°, and decomposes a little above this temperature with evolution of gas.

A. R. L.

Azimides. By R. NIETZKI and N. PRINZ (*Ber.*, **26**, 2956—2960). —When nitrazimidobenzene is reduced with stannous chloride and hydrochloric acid, it yields the corresponding *amidoazimidobenzene*, $NH_2 \cdot C_6H_3 <^{-N}_{NH}> N$, which crystallises from hot water in colourless plates melting at 162°. It forms two series of salts, one with acids as an amido-compound, and one with bases as an azimido-compound. The *dihydrochloride*, the *monhydrochloride*, and the *platinochloride*, $C_6H_6N_4, H_2PtCl_6 + H_2O$, have been prepared, and also the *silver* salt, $C_6H_5N_4Ag$, which is a voluminous, somewhat gelatinous, precipitate. With acetic anhydride, only a *monacetyl* derivative melting at 248° could be obtained.

Amidoazimidobenzene can only be diazotized in strongly acid solution, and is converted by sodium nitrite, under ordinary conditions, into the *azo-derivative*, $N_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(NH_2) \cdot N_3$, which forms yellowish-brown plates, and melts above 300°. Amidoazimidobenzene also very readily combines with other diazo-derivatives, yielding azocolours which closely resemble those obtained in a similar manner from diazobenzene. Thus diazosulphanilic acid yields with amidoazimidobenzene the azo-derivative, $HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3N_3 \cdot NH_2$, which separates in orange-yellow crystals on the addition of sodium acetate. This azo-derivative when subjected to reduction with stannous chloride and hydrochloric acid, yields a new substance which, from

its composition and mode of formation, must be *diamidoazimidobenzene.* It has only been obtained in the form of the *dihydrochloride,*

$$C_6H_7N_5(HCl)_2,$$
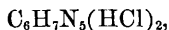
as the free base rapidly oxidises in the air ; the solution of the salt, when treated with an orthodiketone such as croconic acid or glyoxal, yields azines, proving that the two amido-groups are combined with adjacent carbon atoms, the diamidoazimidobenzene having therefore the constitution $\mathrm{{}^{H_2N}_{H_2N}{>}C_6H_2{<}{}^{-\;N}_{NH}{\gg}N}$. Whether the amido-groups occupy the 1 : 2- or 2 : 3-position is uncertain, but the authors regard the latter as the more probable

By the action of nitrous acid on the diamido-compound, the two amido-groups are converted in the usual manner into an azimido-group, *diazimidobenzene,* $\mathrm{N{<}{}^{N\;-}_{NH}{>}C_6H_2{<}{}^{-\;N}_{NH}{\gg}N}$, being formed. After purification, this forms colourless needles melting above 300° ; it is an extremely stable substance, and may be dissolved in concentrated nitric acid, and reprecipitated unaltered by the addition of water.

H. G. C.

Constitution of the Amido-derivatives of Hydroxylamine. By G. MINUNNI and G. ORTOLEVA (*Gazzetta*, **23**, ii, 237—244; compare Minunni, Abstr., 1891, 697).—On heating dibenzhydroxamic acid with phenylhydrazine on the water bath, benzoylphenylhydrazine and a little benzoic acid are obtained. The reaction probably proceeds in two stages, in the first of which benzoylphenylhydrazine and benzhydroxamic acid are formed, whilst in the second stage the latter reacts with more phenylhydrazine, giving the benzoyl derivative and hydroxylamine. On gently heating dibenzhydroxamic acid with aniline, benzanilide is obtained, whilst with paratoluidine the oxamic acid yields benzoylparatoluidide; in these cases also, the action would seem to proceed in two stages. These results can only be explained by assigning the constitution NHBz·OBz to dibenzhydroxamic acid; the formula proposed by Lossen would indicate a very different behaviour under such treatment. W. J. P.

' Diformazyl and its Relations to Diamidrazone. By E. BAMBERGER and F. KUHLEMANN (*Ber.*, **26**, 2978—2982; compare Abstr., 1893, i, 84).—When acids containing the group –CO·CH₂·CH₂·CO– are treated with an excess of alkaline diazobenzene, they are decomposed, with formation of *diformazyl,*

$$N_2HPh\dot{:}C(N_2Ph)\cdot C(N_2Ph)\dot{:}N_2HPh,$$
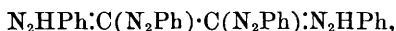
along with other products. Thus levulinic acid,
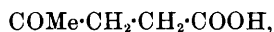
$$COMe·CH_2·CH_2·COOH,$$

yields acetic acid, carbonic anhydride, and diformazyl; acetonediacetic acid (hydrochelidonic acid), $CO(CH_2·CH_2·COOH)_2$, yields the same substance along with carbonic anhydride and succinic acid, whilst the osazone of dihydroxytartaric acid (tartrazin),

$$N_2HPh\dot{:}C(COOH)\cdot C(COOH)\dot{:}N_2HPh,$$
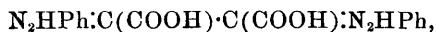
gives this same compound and carbonic anhydride, together with a small amount of other products. Succinic acid itself is not attacked by alkaline diazobenzene.

Diformazyl crystallises in greenish-brown plates, with a surface lustre which varies from yellow to dark green according to the conditions of crystallisation. It melts at 226°, gives a red powder, and forms deep red solutions in organic solvents. It is very readily soluble in benzene, readily in hot alcohol, almost insoluble in light petroleum. With sulphuric acid, it yields a deep, indigo-blue solution. It is a strong base, forming salts which are readily soluble in water, but almost insoluble in dilute acids, so that they are precipitated from aqueous solution by the addition of a few drops of acid. The *sulphate*, $C_{26}H_{22}N_8,H_2SO_4$, forms dark, orange-red needles with a splendid golden-green reflection, and decomposes at 232°; it crystallises well from alcohol and chloroform, in which it is readily soluble. The *hydrochloride*, $C_{26}H_{22}N_8 HCl$, is very similar to the sulphate; it decomposes at 248°. When treated with alcoholic ammonium sulphide, diformazyl is converted into diamidrazone, $N_2HPh:C(NH_2)\cdot C(NH_2):N_2HPh$, identical with that obtained by Senf from phenylhydrazine and cyanogen. This mode of formation is a further proof of the formula proposed for diamidrazone by Bamberger and de Gruyter (this vol., i, 23).   A. H.

Aromatic Oxychlorophosphines. By A. MICHAELIS and G. SCHULZE (*Ber.*, **26**, 2937—2940).—When phosphorus oxychloride and dry aniline hydrochloride are heated together in molecular proportions, together with a little benzene, hydrogen chloride is evolved, and *anilineoxychlorophosphine*, $NHPh\cdot POCl_2$, is formed. The latter is separated from the oily residue by treatment with light petroleum, and it can be purified by recrystallisation from benzene and light petroleum. It forms thick, almost cubic, crystals or needles, melts at 84°, and does not fume in the air; it cannot be distilled without decomposition, and is slowly attacked by cold water, readily by the hot liquid. With alcohols, it forms ethereal salts which are being investigated. *Paratoluidineoxychlorophosphine*, $C_6H_4Me\cdot NH\cdot POCl_2$, is obtained in a similar manner from paratoluidine, and forms thick, white crystals melting at 104°.   H. G. C.

Thioaldehydes and their Conversion into Derivatives of Stilbene. By K. KOPP (*Annalen*, **277**, 339—361; compare Abstr., 1892, 718).—*β-Trithiosalicylaldehyde*, $C_{21}H_{18}S_3O_3$, is prepared by dissolving salicylaldehyde in a well cooled alcoholic solution of hydrogen chloride, treating with hydrogen suphide for $2—2\frac{1}{2}$ hours at $-10°$, and allowing the product to remain for two days; too large a quantity of hydrogen chloride is to be avoided. The compound separates from alcohol in six-sided plates containing 3 mols. C_2H_6O, and, when pure, is colourless and tasteless; it melts at 210°. When iodine is added to its alcoholic solution, the compound remains unaltered; inasmuch, therefore, as all the known α-trithioaldehydes are by this treatment converted into the β-modifications (Baumann and Fromm, Abstr., 1891, 1050), the author's conclusion that his substance is the β-compound

appears justified. The *sodium* derivative, $C_{21}H_{15}S_3O_4Na_3$, crystallises in faintly yellowish leaflets; the *benzoyl* derivative, $C_{42}H_{30}S_3O_6$, melts at 218°. Polymerised *benzoylthiosalicylaldehyde* is obtained by the action of hydrogen sulphide on a 10 per cent. solution of benzoyl-thiosalicylaldehyde in alcohol; the compound melts at 95—98°, and is converted into benzoyl-β-trithiosalicylaldehyde when dissolved in ethylic iodide and heated with iodine.

β-Trithiometahydroxybenzaldehyde, $C_{21}H_{18}S_3O_3$, prepared from meta-hydroxybenzaldehyde in the same manner as the isomeride, forms colourless needles containing 3 mols. C_2H_6O, and melts at 212°; the *benzoyl* derivative melts at 146°. Polymerised *thiomethylmetahydroxy-benzaldehyde* is obtained when an alcoholic solution of methylmeta-hydroxybenzaldehyde is saturated with hydrogen sulphide, and allowed to remain for 1—2 days; it sinters at 90°, and melts at 95—97°. If heated at 160°, or treated with iodine in ethylic iodide solution, *β-trithiomethylmetahydroxybenzaldehyde*, $C_{24}H_{24}S_3O_3$, is produced; it melts at 147°, and becomes brown at 180°.

β-Trithioparahydroxybenzaldehyde, $C_{21}H_{18}S_3O_3$, commences to darken at 165°, and melts at 215°; the *tribenzoyl* derivative melts at 225°.

Benzoylparahydroxybenzaldehyde, OBz·C_6H_4·CHO, melts at 72°, and is converted by hydrogen sulphide into a polymeric benzoylthiopara-hydroxybenzaldehyde melting at 98°, which yields the β-trithio-modification when treated with iodine.

β-Dihydroxystilbene, OH·C_6H_4·CH:CH·C_6H_4·OH [OH:OH = 2:2'], is obtained in small amount on heating β-trithiosalicylaldehyde or the polymeric compound, but more conveniently by warming dibenzoyl-oxystilbene (see below) with alcoholic potash; it crystallises from alcohol in transparent, flat needles having a bluish fluorescence, and melts at 197°. If distilled, it undergoes partial decomposition; the main portion, however, passes over unaltered, whilst a small quantity is converted into α-dihydroxystilbene, m. p. 95° (Harries, Abstr., 1892, 168); the two compounds are separated by taking advantage of the fact that the lower melting isomeride is more volatile with steam than the higher. The conversion of the latter into the former was not accomplished. Attempts to convert stilbene into an isomeride by heating it were unsuccessful. Elbs (Abstr., 1893, i, 272) has observed the existence of two diethoxydinaphthostilbenes, which appear, however, to have different relations to each other from what the dihydroxy-stilbenes have. *β-Dibenzoyloxystilbene*, $C_{28}H_{20}O_4$, already mentioned, is obtained when a small portion of β-trithiobenzoylsalicylaldehyde is rapidly raised to a temperature of 295—305°; it forms colourless needles, melts at 174°, and the *dibromide* melts at 176° with decomposition. Harries describes an isomeric compound (*loc. cit.*).

Diorthomethoxystilbene (see Abstr., 1892, 719).

Dimethoxystilbene, OMe·C_6H_4·CH:CH·C_6H_4·OMe [OMe:OMe = 3:3'], is obtained by distilling polymerised methylthiometahydroxybenz-aldehyde with a large excess of iron powder; it crystallises in rhombic tables, and melts at 99—100°. *Dibenzoyloxystilbene* is formed when β-trithiobenzoylmetahydroxybenzaldehyde is heated at 300°; it melts at 160°.

Paradihydroxystilbene (Elbs and Hoermann, Abstr., 1889, 997) is

obtained in small quantity by heating trithiohydroxybenzaldehyde, or in better yield by hydrolysing its dil enzoyl derivative with alcoholic potash. The last mentioned *dibenzoyl* derivative is formed when polymerised benzoylthioparahydroxybenzaldehyde is heated at 210—220° ; it melts at 238°. A stilbene derivative is not obtained when polymerised benzoylthioparahydroxybenzaldehyde is rapidly heated to 250°.

Diparamethoxystilbene (see Abstr., 1892, 719 ; 1893, i, 272).

<div align="right">A. R. L.</div>

New Synthesis of Coumarone. By G. Komppa (*Ber.*, **26**, 2968—2972).—Coumarone was first obtained by Fittig and Ebert (*Annalen*, **226**, 354), who assigned to it the formula

$$C_6H_4 {<}{\overset{CH}{\underset{-O}{}}}{\gg} CH,$$
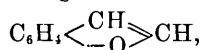
but did not strictly prove its constitution. The accuracy of this formula is proved by the author, who has prepared coumarone synthetically from orthamido-ω-chlorocinnamene, $NH_2 \cdot C_6H_4 \cdot CH{:}CHCl$. This substance has been previously obtained by Lipp (*Ber.*, **17**, 1070), but was not further investigated by him. It crystallises from light petroleum in long prisms melting at 55·5—56·5°, and separates from alcohol in well-formed, monosymmetric crystals. The *platinochloride* forms long, brownish-yellow needles. *Acetylorthamido-ω-chlorocinnamene*, $NHAc \cdot C_6H_4 \cdot CH{:}CHCl$, crystallises in dazzling white, matted needles, melting at 158—159°, and is readily soluble in alcohol. *Orthohydroxy-ω-chlorocinnamene*, $OH \cdot C_6H_4 \cdot CH{:}CHCl$, is obtained by the action of nitrous acid on the amido-compound. It crystallises in long, thick needles melting at 54·5—55·5°, and is readily soluble in alcohol, &c., sparingly in water. It may be preserved for a considerable time in the air without change.

When this hydroxy-compound is dissolved in concentrated aqueous potash, and the solution heated by steam, it is converted, with elimination of hydrogen chloride, into coumarone, which separates as an oil.

The author is endeavouring to prepare the hitherto unknown benzothiophen in a similar manner.

<div align="right">A. H.</div>

Some Derivatives of Methylic Gallate and Dibromogallate. By A. Biétrix (*Bull. Soc. Chim.*, [3], **9**, 692—696).—The bismuth derivative of methylic gallate, $COOMe \cdot C_6H_2(OH)_2 \cdot O \cdot Bi(OH)_2$, is a clear yellow powder, insoluble in water, alcohol, and ether. It is decomposed on melting. The lead derivative, whatever the proportion of lead acetate used to precipitate it, has a nearly constant composition, its formula being

$$COOMe \cdot C_6H_2(OH)[OPbO \cdot C_6H_2(OH)_2 \cdot COOMe]_2.$$
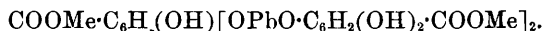
It is a white precipitate, insoluble in water, alcohol, and ether, and blackens on heating.

Methylic lead dibromogallate, $OH \cdot C_6Br_2(O_2Pb) \cdot COOMe$, is precipitated of a greenish-blue colour, rapidly becoming green. It is insoluble in all neutral solvents, and melts with decomposition.

Methylic triacetyldibromogallate, $C_6Br_2(OAc)_3·COOMe$, is formed by heating together acetic chloride and methylic dibromogallate. It is a white compound melting at 150°, insoluble in water, and can be crystallised from boiling alcohol. W. T.

Iodoterephthalic acid and Iodosoterephthalic acid. By H. ABBES (*Ber.*, **26**, 2951—2956).—*Iodoterephthalic acid*, $C_6H_3I(COOH)_2$, is readily prepared by the action of alkaline permanganate on met-iodoparatoluic acid (Abstr., 1893, i, 581), and crystallises from hot water in slender, yellow needles, which in the crude state melt at 274—276°, but sublime when pure. The neutral *sodium, barium,* and *calcium* salts are crystalline and soluble in water, whilst the *silver* salt forms an amorphous, white, insoluble powder. The *dimethylic* salt crystallises from hot water in long. yellowish needles, melts at 77—78°. has an aromatic odour and sharp taste ; the *monomethylic* salt melts at 186°.

Iodoterephthalic acid is converted by the action of fuming nitric acid or of an excess of potassium permanganate into the corresponding *iodosoterephthalic acid*, $IO·C_6H_3·(COOH)_2$, which forms a yellowish precipitate, melts at 260° with evolution of gas, and liberates iodine from potassium iodide solution. It may also be obtained by converting iodoterephthalic acid into the iodochloride, which is a yellow, wax-like mass, and acting on it with a little soda solution. The iodoso-acid only yields salts in which one atom of hydrogen is displaced by metals, the acid *sodium, ammonium, barium,* and *calcium* salts being crystalline, and the *silver* salt a yellow, amorphous mass. The *monomethylic* salt crystallises in white, lustrous plates, and decomposes potassium iodide in the cold. The fact that the iodoso-acid only acts as a monobasic acid, whilst the iodo-acid is bibasic, points to the conclusion that an intramolecular salt formation has taken place in the iodosoterephthalic acid, which may, like iodosobenzoic acid, be represented by the tautomeric formulæ $HO·I—\overset{O—CO}{\underset{}{C_6H_3·COOH}}$ and $IO·C_6H_3(COOH)_2$.

All attempts to replace the amido-group in amidometatoluic acid by iodine were unsuccessful, the corresponding hydroxy-acid being always obtained, whatever method was employed. H. G. C.

Dinitroterephthalic acids. By C. HAEUSSERMANN and E. MARTZ (*Ber*, **26**, 2982—2985).—*Orthodinitroterephthalic acid*

$$[(COOH)_2 : (NO_2)_2 = 1 : 4 : 2 : 3]$$
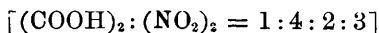
is prepared by heating dinitroparaxylene m. p. 93°, or dinitroparatoluylic acid m. p. 248°, with nitric acid of sp. gr. 1·5 at 170°. It is only slightly soluble in nitric acid, and separates from hot water in well-formed crystals with a vitreous lustre. It melts with decomposition at above 290°, and deflagrates when rapidly heated on platinum foil.

Metadinitroterephthalic acid $[(NO_2)_2 = 3 : 5]$ may be obtained from the dinitroparaxylene m. p. 124°, or from the dinitroparatoluylic

acid m. p. 158°, by oxidation with nitric acid and by the nitration of mononitroterephthalic acid.   It dissolves readily in hot water, forming a yellow solution, and separates on cooling in yellowish, distorted crystals, with a vitreous lustre, which melt at 255° with decomposition.   The *barium salt* is a pale yellow, flocculent mass, and is readily soluble in water.   Separation of barium carbonate takes place when the solution is boiled ; and the salt completely decomposes into barium carbonate and $1:3:5$-dinitrobenzoic acid, when the solution is heated for some time at 200—250°.

The *diethylic salt* forms white, matted needles, which melt at 197° and volatilise with decomposition at a higher temperature.   It is readily soluble in alcohol, sparingly in water.

Paradinitroterephthalic acid $[(NO_2)_2 = 2:5]$ is formed by the oxidation of the dinitroparaxylene m. p. 147—148°, but is best prepared from the paradinitroparatoluic acid m. p. 194°.   It separates from water in small, prismatic crystals with a vitreous lustre, and dissolves readily in hot water, forming an almost colourless solution.   It melts above 280° with vigorous evolution of gas, and deflagrates when heated on platinum foil.   The *barium salt* is a flesh-coloured powder which is readily soluble in water.   The *diethylic salt*, which is rather less soluble in alcohol, ether, and benzene than the corresponding meta-compound, crystallises in lustrous needles, and melts at 144° ; when treated in alcoholic solution with tin and hydrochloric acid, it is converted into diethylic diamidoterephthalate, which was obtained by Baeyer (*Ber.*, **19**, 430) by the oxidation of the diimide of ethylic succinosuccinate.   A. H.

Sulphones from Benzylic Alcohol and Benzoic acid.   By P.
GENVRESSE (*Bull. Soc. Chim.*, [3], **9**, 707—710).—*Dibromditolyl-sulphone*, $SO_2(C_6H_4\cdot CH_2Br)_2$, is obtained by brominating ditolyl-sulphone.   It forms small, white crystals, melts at 108°, and is soluble in hot alcohol and in chloroform.

Dihydroxyditolylsulphone, $SO_2(C_6H_4\cdot CH_2\cdot OH)_2$, is obtained by treating the preceding compound with aqueous potassium carbonate. It forms a mass of fine needles.   It is soluble in alcohol and in boiling water, much less soluble in cold water.   It melts at 156°, and decomposes on further heating.

Dicarboxydiphenylsulphone, $SO_2(C_6H_4\cdot COOH)_2$, is obtained by treating the preceding bromo-compound with potassium permanganate in alkaline solution.   It is a white, crystalline substance, and, though insoluble in water and almost insoluble in alcohol, is very soluble in dilute alkaline solutions.   Its silver salt is obtained as a white precipitate, not blackening in the light.   A pale green copper salt has also been obtained, but has not yet been analysed.   W. T.

Action of Sulphuryl Chloride on Aromatic Hydrocarbons.
By A. TÖHL and O. EBERHARD (*Ber.*, **26**, 2940—2945).—Sulphuryl chloride acts on benzene with formation simply of monochlorobenzene, but if aluminium chloride is added to the mixture, a considerable quantity of benzenesulphonic chloride and a small amount of diphenylsulphone are also obtained.   Toluene is chlorinated by

sulphuryl chloride both in the benzene nucleus and the side chain, but in presence of aluminium chloride the chief product is paratoluenesulphonic chloride, small quantities of parachlorotoluene and paraditolylsulphone being also obtained. Metaxylene and paraxylene behave in a similar manner to toluene, the latter yielding *diparaxylylsulphone*, which crystallises in needles. Mesitylene is attacked by sulphuryl chloride at the ordinary temperature; if, however, the mixture be kept cool, and aluminium chloride then added, chloromesitylene and mesitylenesulphonic chloride are formed. Pseudocumene behaves in a similar manner, but durene, prehnitine, and pentamethylbenzene yield only chlorinated products. Ethylbenzene is converted into parachlorethylbenzene, parethylbenzenesulphonic chloride, and *ethylbenzenesulphone*; the latter crystallises in transparent plates, and melts at 102°. Isopropylbenzene yields the corresponding products, the *isopropylbenzenesulphone* melting at 109—110°. Cymene yields only resinous products, whilst naphthalene is converted chiefly into α-chloronaphthalene and a small quantity of α-naphthalenesulphonic chloride. H. G. C.

The Strength of Orthosulphobenzoic acid. By J. SHIELDS (*Ber.*, **26**, 3027—3028).—The author points out that the formation of ammonium orthosulphobenzoate by heating orthosulphobenzoic acid with ammonium chloride in concentrated solution simply proves that this acid is less volatile than hydrochloric acid, but not that it is a stronger acid, as stated by Jesurun (Abstr., 1893, i, 715). A determination of the relative strength of the acids must necessarily take into account the law of mass action. J. B. T.

Diketohydrindene. By W. WISLICENUS and F. REITZENSTEIN (*Annalen*, **277**, 362—374).—*Triketohydrindene-β-hydrazone*,

$$C_6H_4{<}{{CO}\atop{CO}}{>}C{:}N{\cdot}NHPh,$$
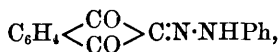
is precipitated when diketohydrindene is dissolved in the smallest possible quantity of dilute soda and a solution of diazobenzene chloride together with sodium acetate added; it crystallises from aqueous alcohol in orange-yellow, prismatic needles, melts at 190°, and dissolves in concentrated sulphuric acid with a red colour, which remains unchanged on adding a drop of ferric chloride solution, but changes first to blue and subsequently to reddish-violet on the addition of potassium dichromate. When ether is added to its solution in alcoholic soda, the *sodium* salt separates as a reddish-yellow precipitate.

When an alcoholic solution of benzylidenediketohydrindene (*Annalen*, **252**, 75) is treated with phenylhydrazine, benzaldephenylhydrazone is obtained, together with the mono- and di-hydrazone of diketohydrindene.

It has been shown (*Annalen*, **252**, 72) that when diketohydrindene is heated by itself or boiled with water, a condensation product, anhydrobidiketohydrindene, $C_{18}H_{10}O_3$, is formed; the authors have confirmed this formula by the cryoscopic method, and the following experiments render it probable that the compound has the constitution

$C_6H_4 {<}{CO \atop CO}{>} C{:}C {<}{C_6H_4 \atop CH_2}{>} CO$. It dissolves in sodium hydroxide solution with an intense red colour, which differs from that exhibited by phenolphthaleïn in that the colour is not destroyed by excess of alkali. When the alkaline solution is evaporated, the residue taken up with alcohol, the alcoholic solution evaporated, and the residue triturated with alcohol, the *sodium* salt, $C_{18}H_9O_3Na$, is obtained as a dark, brownish-red powder; the *calcium* salt, $(C_{18}H_9O_3)_2Ca$, is a bluish-black precipitate; and the *copper* salt an almost black precipitate. The *oxime*, $C_{18}H_{10}O_2{:}NOH$, crystallises in small, yellow needles, commences to darken at 210°, and decomposes above this temperature without previously melting; whilst its *acetyl* derivative forms yellow leaflets, and decomposes above 180°. When anhydrobidiketohydrindene is suspended in absolute alcohol, and phenylhydrazine (4 mols.) added, diketohydrindenediphenylhydrazone, $C_6H_4 {<}{C(N_2HPh) \atop C(N_2HPh)}{>}CH_2$ (m. p. 171—172°) is obtained; but if less phenylhydrazine (1 mol.) is used, diketohydrindenemonophenylhydrazone is formed. When anhydrobidiketohydrindene is treated with concentrated sulphuric acid at the ordinary temperature, or with acetic anhydride at 150—160°, further condensation takes place, and a red compound, $(C_{18}H_8O_2)_n$, which does not melt at 310°, is produced.   A. R. L.

Symmetrical β-Diketones of the Aromatic Series. By A. Béhal and V. Auger (*Bull. Soc. Chim.*, [3], **9**, 696—704).

—Malonic chloride reacts with aromatic hydrocarbons in presence of aluminium chloride to give a diketone of the type $R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R$, a ketone of the type $R{\cdot}COMe$, and a hydrocarbon. The diketones act as acids, forming metallic derivatives. They are crystalline substances, insoluble in water, but soluble in aqueous solutions of alkalis and in organic solvents. Their stability appears to incı ease with the number of carbon atoms in the molecule; the lower members of the series, such as dibenzoylmethane, are readily decomposed by alkalis into ketones and acids.

Dituluylmethane, $CH_2(CO{\cdot}C_6H_4Me)_2$ [Me : CO = 1 : 4], is prepared by the action of malonic chloride on toluene. It melts at 126°. It is very soluble in benzene but only sparingly so in absolute alcohol, from which it is deposited in long needles; its alcoholic solution becomes violet on adding ferric chloride, and on diluting with water, a red, crystalline powder of the ferric salt is deposited. It is decomposed by concentrated soda into paramethylbenzoic acid and methylphenyl methyl ketone.

Diethylbenzoylmethane, $CH_2(CO\,C_6H_4Et)_2$ [Et : CO = 1 : 4], resembles the above in mode of preparation and in properties. It melts at 42°. When decomposed by soda, it yields parethylbenzoic acid and ethylphenyl methyl ketone; the latter has a sp. gr. 0·9719 and an odour of aniseed. The hydrocarbon produced along with this diketone is metadiethylbenzene (compare Abstr., 1890, 493).

Diortho xyloylmethane, $CH_2(CO{\cdot}C_6H_3Me_2)_2$ [Me₂ : CO = 1 : 2 : 4], melts at 138°. It is attacked by soda with difficulty, and resembles

the preceding compounds in its products of decomposition and properties. It gives a brown coloration with ferric chloride.

Dimetaxyloylmethane [$Me_2 : CO = 1 : 3 : 4$] is very soluble in acetic acid or alcohol. It forms prisms melting at 82°. With ferric chloride, it gives a red coloration, becoming more violet on the addition of water. In its properties and mode of decomposition by soda, it resembles the foregoing compounds.

Diparaxyloylmethane [$Me_2 : CO = 1 : 4 : 3$], boils in a vacuum at about 250°. It is very soluble in benzene and light petroleum, but only sparingly in 95 per cent. alcohol. It forms small crystals melting at 101—102°. With very concentrated soda, it produces the corresponding dimethylbenzoic acid and dimethylphenyl methyl ketone [$Me_2 : CO = 1 : 4 : 3$], boiling at 225° under 764 mm. pressure, and having a sp. gr. = 1·0154 at 0°.

Dimesitoylmethane, $CH_2(CO·C_6H_2Me_3)_2$ [$Me_3 : CO = 1 : 3 : 5 : 2$], melts at 96—97°. It requires to be heated at 300° in a sealed tube with soda, and then yields a trimethylphenyl methyl ketone and isodurylic acid. It gives a red coloration with ferric chloride in alcoholic solution.

A diketone from cymene has been obtained as an impure liquid. With soda, in a sealed tube at 300°, it gave, in addition to an acid which was not examined further, a ketone of agreeable odour, boiling at 240°, and yielding an oxime boiling at 176° (21 mm.) and melting at 84°. No diketone has been obtained in a pure state from naphthalene by means of this reaction.   W. T.

Physical Modification of β-Carbodiphenylimide and β-Carbodiparatolylimide. By C. Schall (*Ber.*, **26**, 3064—3065).—When β-carbodiphenylimide is carefully heated to its melting point and then suddenly and strongly cooled, it solidifies to a yellowish, amorphous mass, which melts at a lower temperature and is more soluble than the β-modification. When slowly heated, it melts at 96—99°, and at 108—130° is reconverted into the β-modification melting at 158—160°.

β-Carbodiparatolylimide, when heated and cooled in the same way, is at first semi-fluid, but after a time solidifies. It now melts at 60—70°, and cannot be reconverted into the β-modification by further heating.

Triparatolylguanidine, when heated and quickly cooled, melts at 46—50°, and at 70—80° is reconverted into the ordinary modification, melting at 123—124°.

A similar behaviour is shown by the compound obtained from β-carbodiphenylimide and phenylhydrazine. The new modification is always amorphous, even if the primary compound is crystalline and pure.   E. C. R.

Two Recent Publications on the Benzileoximes. By G. Minunni and G. Ortoleva (*Gazzetta*, **23**, ii, 244—248).—This paper deals with the criticisms of Auwers and Siegfeld (Abstr., 1893, i, 354) and of Claus (Abstr., 1893, i, 355) on the authors' work (Abstr., 1893, i, 97).   W. J. P.

Reduction Products of Benzilehydrazone. By A. PURGOTTI (*Gazzetta*, **23**, ii, 225—231).—In a previous preliminary note (Abstr., 1893, i, 354), the author described a new base, obtained by reducing benzilehydrazone; the supposition that the base is amidodibenzile is now confirmed. Small quantities of aniline and dibenzile are also produced.

Amidodibenzile, $CH_2Ph\cdot CHPh\cdot NH_2$, is an oil having an aromatic odour, and boiling without appreciable decomposition at 310—311° under 750 mm. pressure. It is very soluble in alcohol, ether, chloroform, or carbon bisulphide, but only sparingly in water. Its *hydrochloride* crystallises in small, white needles melting at 242—243°, and the *platinochloride* in golden scales which melt at about 188°. The *oxalate* is obtained as a white, crystalline precipitate melting at 158°; the *picrate* melts at 190°.

The constitution of the base is established by the fact that on treating the hydrochloride with silver nitrite, phenylbenzylcarbinol is obtained.

Diphenylethyloxamide, $(CH_2Ph\cdot CHPh\cdot NH)_2C_2O_2$, is prepared by heating the base on the water bath with an ethereal solution of ethylic oxalate. It forms white needles melting at 212°, and is soluble in chloroform or boiling benzene, but sparingly so in ether, alcohol, or water.

Acetamidodibenzile, $CH_2Ph\cdot CHPh\cdot NHAc$, obtained by heating amidodibenzile hydrochloride with acetic anhydride and fused sodium acetate, crystallises in white needles melting at 147—148°.

Dibenzilecarbamide, $CH_2Ph\cdot CHPh\cdot NH\cdot CO\cdot NH_2$, is prepared by the action of potassium cyanate on the hydrochloride described above; it forms small, white crystals which melt at 98°, and is soluble in alcohol, ether, benzene, or chloroform.   W. J. P.

Action of β-Naphthol and α- and β-Naphthylamines on the Nitrobenzaldehydes. By M. ZENONI (*Gazzetta*, **23**, ii, 215—224).—The behaviour of β-naphthol towards aliphatic aldehydes has been studied by Hosaeus and by Abel (Abstr., 1893, i, 100, 172); the present paper gives the results obtained with the nitrobenzaldehydes.

On adding a little sulphuric acid to an acetic acid solution of orthonitrobenzaldehyde and β-naphthol, *orthonitrobenzal-β-dinaphtholmethane*, $NO_2\cdot C_6H_4\cdot CH(C_{10}H_6\cdot OH)_2$, is slowly deposited; it forms a crystalline mass melting at 207°, is soluble in ether, chloroform, or acetone, but insoluble in benzene and in light petroleum. The corresponding *oxide*, $NO_2\cdot C_6H_4\cdot CH{<}^{C_{10}H_6}_{C_{10}H_6}{>}O$, is obtained by boiling the acid solution during the preparation of the previous substance. It forms beautiful, pale green, acicular crystals which turn brown above 250°; it is sparingly soluble in the ordinary solvents.

Metanitrobenzal-β-dinaphtholmethane is prepared in a similar manner to its ortho-isomeride; it melts at 184°, and, on boiling with potash, yields an unstable substance which crystallises in beautiful golden scales. The dinaphthol derivative yields a crystalline *diacetyl* derivative which melts at 242°, and is very sparingly soluble in the ordin-

ary solvents. The *oxide* is obtained in silvery white scales melting at 220°.

Orthonitrobenzal-β-dinaphtholmethane could not be prepared, the *oxide* being obtained instead; this substance forms small, yellow needles which turn brown when heated above 260°.

On mixing acetic acid solutions of α-naphthylamine and meta-nitrobenzaldehyde, *metanitrobenzal-α-dinaphthylamine*,

$$NO_2 \cdot C_6H_4 \cdot CH(C_{10}H_6 \cdot NH_2)_2,$$
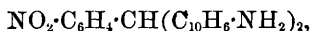
separates. It is very soluble in ether or chloroform, and forms yellow laminæ melting at 102—103°. The isomeric *para*-derivative is obtained in yellow needles melting at 161—162°, and the *ortho*-isomeride melts at 119—120°. The *meta*-derivative, obtained from β-naphthyl-amine, forms yellow crystals melting at 90—91°; the *para*-isomeride is obtained in yellow needles melting at 120—121°, whilst the *ortho*-derivative forms yellow crystals melting at 92—93°, and is very sensitive to light. These derivatives of the naphthylamines may also be prepared by boiling the alcoholic solutions of the two constituents. If, however, fuming hydrochloric acid is added to the alcoholic solutions before boiling, *nitrophenylhydronaphthacridines* are obtained; these will be subsequently studied.   W. J. P.

A Naphthylene Diazosulphide. By P. JACOBSON and C. SCHWARZ (*Annalen*, **277**, 257—261; compare this vol., i, 123).—It has been stated (Abstr., 1888, 1307) that 2 : 1-ethenylamidonaphthyl mercaptan melts at 81°. The authors find that the melting point of the compound is not sharp, and, even after repeated recrystallisation from aqueous alcohol, it softens at 68—70°, and melts at about 80°; if, however, the crystals are kept over concentrated sulphuric acid in a partial vacuum, they effloresce and then melt sharply at 48°. When the compound is heated with phthalic anhydride and zinc chloride, a *phthalone* melting above 300° is formed. When the ethenyl base is heated at 220—230° with aqueous potash, the product dissolved in water, sodium nitrite added, and the solution treated in the cold with dilute sulphuric acid, *naphthylene diazosulphide*, $C_{10}H_6 {<}{\overset{N}{\underset{S}{}}}{>}N$ [N : S = 1 : 2], is obtained; it crystallises in small needles, having a bronzy lustre, melts at 89°, appears to decompose on exposure to light, and resembles phenylene diazosulphide in its behaviour.

                                        A. R. L.

β-Naphtholcarboxylic acid (m. p. 216°) and its Derivatives. By S. ROBERTSON (*J. pr. Chem.*, [2], **48**, 534—536).—β-Naphtholcarb-oxylic acid (m. p. 216°) was prepared by heating sodium β-naphth-oxide with liquid carbonic anhydride at 270—280° in an autoclave. The product is converted into the ammonium salt, and then, by the action of phosphorus pentachloride, into the chloride, which, by treatment with boiling water, is converted into the pure acid. When treated with nitric acid, it yields, according to the conditions of working, either a mononitro or dinitro acid.

The *mononitro-acid*, $NO_2 \cdot C_{10}H_5(OH) \cdot COOH$, crystallises in lustrous, golden-yellow prisms, melts at 233—238° with decomposition, and,

when boiled with water, decomposes with evolution of carbonic anhydride. The *sodium, ammonium,* and *potassium salts* are described ; they are anhydrous, and give insoluble microcrystalline precipitates with salts of the heavy metals. The *ethylic salt* crystallises in lustrous, greenish needles, melts at 160°, and is easily hydrolysed by cold alkalis.

Amido-β-naphtholcarboxylic acid crystallises in colourless, lustrous needles, decomposes before melting with the formation of a red dye, and yields dihydroxynaphthalenecarboxylic acid when boiled with acids. The *hydrochloride* crystallises in white, lustrous needles, and is hydrolysed by water or alcohol. *Diazonaphtholcarboxylic acid,* $OH \cdot C_{10}H_5 <^{—\ N}_{COO} \gg N$, crystallises in long, brownish-yellow needles. *Chloronaphtholcarboxylic acid* melts at 230°. *Dihydroxynaphthalenecarboxylic acid,* obtained by decomposing the diazo-compound with sulphuric acid, crystallises in long, greenish needles.

Dinitronaphtholcarboxylic acid crystallises in bright yellow, lustrous needles, melts at 252° with decomposition, but begins to decompose at 242°. The *ethylic salt* crystallises in white, prismatic needles, and melts at 198°.   E. C. R.

β-**Naphtholcarboxylic acid (m. p. 216°).** By R. MÖHLAU (*Ber.,* **26**, 3065—3067; compare also S. v. Kostanecki, this vol., i, 91).— Naphthaleneazo-β-hydroxynaphthoic acid, obtained by the action of diazonaphthalene chloride on β-naphtholcarboxylic acid (m. p. 216°), yields, on reduction, amido-β-hydroxynaphthoic acid. The latter is converted by boiling with dilute sulphuric acid into the same β-naphthoquinolcarboxylic acid as that which is obtained by the action of carbonic anhydride on sodium β-naphthoquinol ; it crystallises in yellow leaflets, melts at 207° with decomposition, and gives a green coloration with ferric chloride.

β-*Amidonaphthoic acid* is obtained by heating the β-naphtholcarboxylic acid with aqueous ammonia at 260—280°. It crystallises in lustrous, yellow leaflets, melts at 211—212°, and yields phthalic acid when oxidised with potassium permanganate. The diazosulphate, $COOH \cdot C_{10}H_6 \cdot N_2 \cdot HSO_4$, when treated with copper powder in alcoholic solution, yields β-naphthoic acid, which melts at 181—182°.

These reactions prove that the β-naphtholcarboxylic acid melting at 216° is the 2 : 3-compound.   E. C. R.

Relative Stability of certain Sulphonic Derivatives of Naphthalene. By P. FRIEDLAENDER and P. LUCHT (*Ber.,* **26**, 3028—3034).—The authors have investigated the relative ease with which the sulphonic group of a number of naphthalene derivatives is replaced by hydrogen ; the naphthol derivatives were treated in dilute acid, the naphthylamine derivatives in dilute alkaline, solution at ordinary temperatures with sodium amalgam. The following compounds are practically unaltered :—β-Naphthalenesulphonic acid, α-naphtholsulphonic acid 1 : 2, β-naphtholsulphonic acids 2 : 3' and 2 : 2'. The following are slowly changed :—α-Naphtholsulphonic acids 1 : 3 and 1 : 2'. α-Naphthalenesulphonic acid, α-naphtholsulph-

onic acids 1 : 4, 1 : 4′, 1 : 1′, and β-naphtholsulphonic acid 2 : 1′, are all readily attacked by sodium amalgam. α-Naphtholdisulphonic acids 1 : 2 : 4 and 1 : 4 : 2′ are converted into sulphonic acids. α-Naphtholtrisulphonic acid 1 : 2 : 4 : 2′ yields the disulphonic acid 1 : 2 : 2′. β-Naphtholdisulphonic acids 2 : 3′ : 1′ and 2 : 3 : 1′ are converted into the sulphonic acid 2 : 3′. The following naphthylamine-sulphonic acids are readily reduced :—α-Naphthylaminesulphonic acids 1 : 4, 1 : 4′, 1 : 1′, β-naphthylaminesulphonic acids 2 : 4′ and 2 : 1′. α-Naphthylamine-ε-disulphonic acid 1 : 3 : 1′ is rapidly converted into the 1 : 3-acid. β-Naphthylaminedisulphonic acid 2 : 4 : 1′ yields β-naphthylamine. The α-sulphonic acids 1 : 2, 1 : 3, 1 : 2′, and the β-acids 2 : 3′ and 2 : 2′ are much more stable.

2 : 3′-Naphthylenediamine is prepared by the reduction of the nitro-sulphonic acid from 2 : 1′-β-naphthylaminesulphonic acid, and subsequent elimination of the sulphonic group; it crystallises from water in colourless plates, darkens in air, and melts at 216°. With ferric chloride, a green coloration is obtained, which becomes blue on warming. Chromic anhydride, bromine water, and calcium hypochlorite all produce a dark green coloration which changes to brown. The *diacetyl derivative* is crystalline. The original acid, therefore, has the constitution $[NH_2 : SO_3H : NO_2 = 2 : 1′ : 3′]$. In a similar manner it is shown that the naphthylenediaminesulphonic acid from α-naphthylaminedisulphonic acid 1 : 4 : 3′ yields 1 : 3′-naphthylene-diamine, and that its constitution is $[NH_2 : SO_3H : NH_2 = 1 : 4 : 3′]$. 1 : 3′-Dihydroxynaphthalene-4-sulphonic acid and 3′ : 1-amido-naphthol-4-sulphonic acid yield respectively 1 : 3′-dihydroxy-naphthalene and an amidonaphthol, which has not yet been described. The following β-sulphonic acids are not decomposed by sodium amalgam :—1 : 1′-Dihydroxynaphthalene-3 : 3′-disulphonic acid, 2 : 3-dihydroxynaphthalene-3′-sulphonic acid, 1 : 1′-diamido-naphthalene-3 : 3′-disulphonic acid, and 2 : 1′-amidonaphthol-3′-sulphonic acid. α-Sulphonic acids are, therefore, much more easily and completely reduced at ordinary temperatures than β-sulphonic acids.

J. B. T.

Dihydroanthrol and Dihydroanthramine. By E. BAMBERGER and F. HOFFMANN (*Ber.*, **26**, 3068—3072).—In accordance with Bamberger's centric hypothesis, anthrol and anthramine are capable of taking up only two hydrogen atoms, and these combine with the central carbon atoms and the six-carbon atom rings become benzene rings. The properties of dihydroanthrol and dihydroanthramine are in accordance with this hypothesis ; they show the typical properties of phenol and aniline respectively.

Dihydroanthrol, $C_6H_4{<}^{CH_2}_{CH_2}{>}C_6H_3 \cdot OH$, is obtained by reducing anthrol with sodium and absolute alcohol. A small quantity of anthracene dihydride which is formed is separated by steam distillation, and the filtered solution is then precipitated with acid. It crystallises in white, lustrous plates, melts at 129·5°, and dissolves in sodium hydroxide with a yellow coloration and green fluorescence. It gives a yellow solution with concentrated sulphuric acid, which, on heating, turns greenish-yellow and then violet. It yields a raspberry-

red dye with diazosulphanilic acid.   It sublimes, when heated at 200°, in a current of carbonic anhydride. and is slowly volatile with steam. Unlike anthrol, it is not altered by boiling with alcohol and hydrochloric acid, or by heating with ammonia or with acetamide.   The *acetyl compound* is a yellow, crystalline powder, melts at 148°, and dissolves in alcohol with a blue fluorescence.   It gives a golden-yellow solution with concentrated sulphuric acid, which, on heating, turns green and then dark violet.   The *benzoyl compound* crystallises in bright yellow nodules, and melts at 124°.   The *ethoxy-compound*, $C_6H_4:C_2H_4:C_6H_3\cdot OEt$, obtained by warming dihydroanthrol with ethylic iodide, potassium hydroxide, and absolute alcohol, crystallises in white aggregates, and melts at 107°.   Dihydroanthrol is not altered by boiling with amyl alcohol and sodium.

Dihydroanthramine, $C_6H_4\!<^{CH_2}_{CH_2}\!>C_6H_3\cdot NH_2$, has already been described by Liebermann and Bollert   (*Ber.*, **15**, 853).   Unlike anthramine, which is intensely yellow and is a feeble base, it is colourless, and readily dissolves in very dilute acids.   When treated with nitrous acid, it yields a *diazo-compound*, which gives intensely coloured dyes with aromatic bases and phenols, and when distilled with steam, is converted into dihydroanthrol.   E. C. R.

Isomerism in the Terpene Series.   By O. WALLACH (*Ber.*, **26**, 3072—3077).—The author gives an explanation of the relations between limonene (or dipentene) derivatives and terpinol which accounts for the dihydrohalogen additive products of limonene being inactive, whilst some limonene hydrochlor-nitrolamines are active. An asymmetric carbon atom always occurs in the latter, and not in the former, on this interpretation.   J. W.

Volatile Hydrocarbons in Essence of Valerian.   By OLIVIERO (*Compt. rend.*, 117, 1096—1097).—That fraction of the volatile hydrocarbons from essence of valerian which boils at about 157° consists partly of a terebenthene and partly of a camphene, which can be separated by the action of alcoholic potassium acetate on the monhydrochlorides.   This camphene is lævogyrate ($[\alpha]_D = -21°$), and yields a monhydrochloride which is dextrogyrate.

The monhydrochloride of the terebenthene has a specific rotatory power $[\alpha]_D = -25°$.   The camphene and terebenthene are accompanied by a small quantity of a feebly lævogyrate citrene.
                                   C. H. B.

Presence of Camphene in Oil of Spike.   By G. BOUCHARDAT (*Compt. rend.*, 117, 1094—1096).—Oil of spike consists almost entirely of camphor, linalol, and a small quantity of borneol and its isomerides. but also contains a small quantity of a hydrocarbon, $C_{10}H_{16}$, which boils at 158—160°, and has all the properties of the camphenes.   Its rotatory power is $+29°$ 10', and it yields a monhydrochloride with a rotatory power of $-20°$ 15'.   This hydrochloride is decomposed when heated with an alcoholic solution of potassium acetate, and the hydrocarbon itself, when heated at 100° with glacial formic acid, yields borneol formate, together with some diterpilene, which is probably

derived from a small quantity of terebenthene associated with the camphene.

It is noteworthy that borneol and a camphene occur together, according to Oliviero, in essence of valerian, and are both lævogyrate, whilst in oil of spike they are both dextrogyrate. In both cases the camphene doubtless results from the decomposition of ethereal derivatives of borneol, either during the life of the plant or by simple distillation with water.   C. H. B.

New Source of Rhodinol. By P. MONNET and P. BARBIER (*Compt. rend.*, 117, 1092—1094).—When oil of pelargonium is subjected to careful fractional distillation under reduced pressure, it yields *rhodinol*, $C_{10}H_{17}\cdot OH$, identical in all its physical and chemical properties with the rhodinol obtained from oil of roses; it boils at 124° under a pressure of 14 mm.; sp. gr. at 0° = 0·8886; refractive index $n_r = 1\cdot4652$ and $n_b = 1\cdot4789$ at 16·7°; specific rotatory power $[\alpha]_D = -2°\ 34'$.   C. H. B.

Constitution of Camphor and its Derivatives. By J. BREDT (*Ber.*, 26, 3047—3057).—The products of the oxidation of camphor with nitric acid are camphoric acid, $C_{10}H_{16}O_4$, camphanic acid, $C_{10}H_{16}O_5$, and camphoronic acid, $C_9H_{14}O_6$. They form a graduated series : thus camphoronic acid is obtainable by the oxidation of camphoric and camphanic acids, and camphanic acid is formed by the oxidation of camphoric acid. Camphoronic acid is a tribasic acid, somewhat resembling tricarballylic acid in its behaviour; when subjected to prolonged distillation it yields carbonic anhydride, water, carbon, isobutyric acid, trimethylsuccinic acid, and small quantities of bye-products resembling phorone. From these results the author assigns to camphoronic acid the constitution

$$COOH\cdot CMe_2\cdot CMe(COOH)\cdot CH_2\cdot COOH,$$
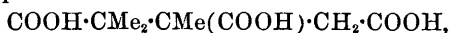
and thence deduces the following constitutional formulæ : camphoric acid,

$$\begin{array}{c} CH_2\text{———}CH_2 \\ | \qquad\qquad | \\ COOH\cdot CMe\cdot CMe_2\cdot CH\cdot COOH \end{array} \;;\; \text{camphanic acid,}$$

$$CMe\!\!\left\langle\begin{array}{c} CH_2\cdot CH_2 \\ - CMe_2 - \\ CO\text{——}O \end{array}\right\rangle\!\!C\cdot COOH \;;$$
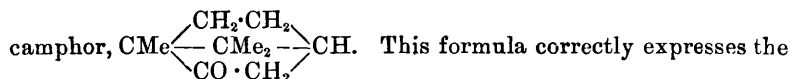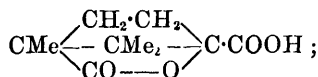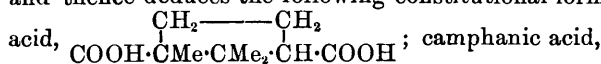
camphor, $CMe\!\!\left\langle\begin{array}{c} CH_2\cdot CH_2 \\ - CMe_2 - \\ CO\cdot CH_2 \end{array}\right\rangle\!\!CH.$ This formula correctly expresses the reaction of camphor and its derivatives. Thus it explains the formation of bromocamphoric acid, and its conversion into camphanic acid; the production of dinitrocaproic acid by the prolonged action of nitric acid on camphor; the formation of cymene from camphor, and of isopropylsuccinic acid from camphoric acid, &c. The author gives constitutional formulæ explaining these reactions.

According to the author's formula, only two isomeric camphenes are possible, namely, $CMe\!\!\left\langle\begin{array}{c} CH_2\cdot CH_2 \\ - CMe_2 - \\ CH:CH \end{array}\right\rangle\!\!CH$ and $CMe\!\!\left\langle\begin{array}{c} CH_2\cdot CH_2 \\ - CMe_2 - \\ CH_2\cdot CH \end{array}\right\rangle\!\!C.$
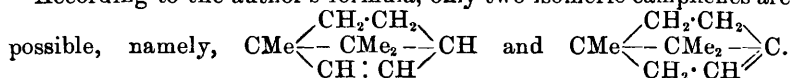
The second formula then expresses the constitution of pinene, and from this the constitution of terpin is expressed by the formula

$OH \cdot CMe < ^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2} > C(OH) \cdot CHMe_2$, which is the formula assigned

to terpin by Wallach (Abstr., 1891, 1081) and v. Baeyer (*Ber.*, **26**, 2564).   E. C. R.

Heat of Neutralisation of Camphoric acid. By G. MASSOL

(*Bull. Soc. Chim.*, [3], **9**, 719—721).—Purified camphoric acid, m. p. 180°, has a solubility in water at 8° of 4·2 grams per litre ; its solution is accompanied by absorption of heat : 1·87 Cal. (200 grams in 24 litres). The heat of neutralisation by soda is 27·16 Cal., 13·77 and 13·39 Cal being developed for the first and second equivalents respectively (solid acid dissolved in soda solution).

Sodium hydrogen camphorate is not obtained by the spontaneous evaporation of its solution, but varying mixtures of normal and acid salts. The heat of solution of anhydrous sodium hydrogen camphorate (222 grams in 10 litres) is $+4·37$ Cal.

Normal sodium camphorate crystallises with $5H_2O$; the anhydrous salt is very soluble in water with development of heat, $+15·77$ Cal. (244 grams in 8 litres).

Heat of formation of the salts in the solid state—

$C_{10}H_{16}O_4$ sol. $+$ NaOH sol. $= C_{10}H_{15}NaO_4$ sol. $+$
    H_2O sol................................... $+18·74$ Cal.
$C_{10}H_{15}NaO_4$ sol. $+$ NaOH sol. $= C_{10}H_{14}Na_2O_4$ sol.
    $+ H_2O$ sol. .... $+13·20$ „
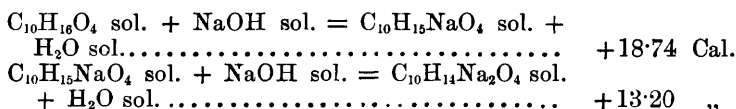
The total heat of formation of the sodium salt, $+31·94$ Cal., is much less than with other bibasic organic acids ; that of the acid salt is sensibly equal to the average heat of formation of the corresponding salts of the monobasic fatty acids.   W. T.

Datiscin and its Decomposition Products. By E. SCHUNCK

and L. MARCHLEWSKI (*Annalen*, **277**, 261—276).—Datiscin was prepared by extracting the bruised roots of *Datisca cannabina* with dilute alcohol, distilling off the alcohol, extracting the residue with water, treating the aqueous solution with a small quantity of lead acetate (basic ?), and concentrating the filtrate, from which datiscin separates on cooling. It is repeatedly recrystallised from boiling water, when the crystals have but a faintly yellow tint. In its general properties, datiscin agrees with Stenhouse's description (*Annalen*, **98**, 167) ; it is very sparingly soluble in ether, and melts at 190°. Air-dried datiscin gave, on analysis, values agreeing with the formula $C_{21}H_{24}O_{11} + 2H_2O$, and that dried at 130° gave values agreeing with the formula $C_{21}H_{24}O_{11} + H_2O$. Specimens which had been dried at the latter temperature, however, were frequently found to have undergone decomposition.

When datiscin is boiled with dilute sulphuric acid, datiscetin separates from the solution on cooling, and a sugar, which is not glucose, as Stenhouse supposed, but rhamnose, remains dissolved. The rhamnose was identified by elementary analysis and by its melting

point (91°), as well as by means of its osazone and sodium compound.

Datiscetin, $C_{15}H_{12}O_6$, crystallises from alcohol in bright yellow needles, melts at 237° (uncorr.), and dissolves in concentrated sulphuric acid, forming a yellow solution, which subsequently exhibits a beautiful blue fluorescence. The above formula was confirmed by determinations of the molecular weight by the ebulloscopic method. The lead salt has the composition $C_{15}H_{10}O_6Pb$. When datiscetin is fused with potash, salicylic acid is formed. The authors confirm Stenhouse's observations that datiscetin is converted into picric acid on treatment with concentrated nitric acid, and into nitrosalicylic acid (m. p. 226°), on treatment with dilute nitric acid. They conclude that the nitrosalicylic acid has the constitution [COOH : OH : NO₂ = 1 : 2 : 5]. It appears probable that when datiscetin is distilled with zinc dust methyldiphenylenic oxide is formed, whilst if boiled with hydriodic acid (sp. gr. 1·7), methylic iodide is produced, together with a *compound* melting at 130°, and having the composition of a tetrahydroxy-xanthone, $C_6H_4{<}^{CO}_{CO}{>}C_6(OH)_4$. Taking the whole of the above-described facts into account, the authors submit the formula $C_6H_4{<}^{CO}_{CO}{>}C_6(OMe)_2(OH)_2$ [$(OMe)_2 : (OH)_2 = 1 : 2 : 3 : 4$] as representing the probable constitution of datiscetin.　　　A. R. L.

Santonin. By A. ANDREOCCI (*Ber.*, **26**, 2985—2986).—The formula for santonin, which, according to Klein (*Ber.*, **26**, 2506), the author has quoted (Abstr., 1893, i, 526) incorrectly from the paper by Cannizzaro and Gucci, on "Some derivatives of Photosantonic acid" (*Real. Accad. Linc.*, 1892, ii, 149), accurately expresses all that has been proved concerning the constitution of santonin, and only differs from that put forward by Cannizzaro in the nature of the lactone combination, which is acknowledged by the last named chemist to be still an open question.　　　A. H.

Santonone. By G. GRASSI-CRISTALDI (*Ber.*, **26**, 2988—2990).— The author points out that Klein (this vol., i, 51) is in error in employing the formula $(C_{15}H_{18}O_2)_2$ for santonone instead of $(C_{15}H_{17}O_2)_2$, and further maintains the accuracy of his original observation that the melting point of santonone is 223°, and not 200—201° as stated by Klein. The resulting questions raised by Klein will be found answered in the author's original communication on the subject (Abstr., 1893, i, 110).　　　A. H.

Oxidation of Piperidine and of α-Pipecoline by Hydrogen Peroxide. By R. WOLFFENSTEIN (*Ber.*, **26**, 2991—2998; compare Abstr., 1892, 1484).—Amidovaleraldehyde, prepared in the manner previously described, on extraction with ether from acid solution, forms crystals which melt at 39° and boil at 110—111° under 55 mm. pressure. The *phenylhydrazone acetate*, $C_{13}H_{21}N_3O_2$, is crystalline and melts at 130°. By the action of hydrogen peroxide in excess on piperidine, formic and butyric acids are formed in addition to glutaric acid. On reducing amidovaleraldehyde with zinc and

hydrochloric acid, piperidine is regenerated. With nitric acid, the aldehyde forms a *nitrate*, but the slightest excess of acid converts the aldehyde into succinic acid. *α-Piperidinesulphonic acid*, $C_5NH_{10}\cdot SO_3H$, is formed from sodium hydrogen sulphite and amidovaleraldehyde hydrochloride, and crystallises in prismatic needles melting at 180°. The compound has no reducing properties and does not react with iodine and starch; on heating with fuming nitric acid and barium chloride, barium sulphate is precipitated. The *sodium salt* is readily soluble, and is formed from sodium hydrogen sulphite and amido-valeraldehyde.

Amidocaproaldehyde, $NH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHO$, is prepared by the action of hydrogen peroxide on α-pipecoline at ordinary temperatures for 48 hours. It boils at 116—117° under 60 mm. pressure, and closely resembles amidovaleraldehyde in properties and reducing powers. The *hydrochloride*, $C_6H_{13}NO,HCl$, which can be crystallised from a mixture of acetone and alcohol, melts at 116°. By the prolonged action of hydrochloric acid on amidocaproaldehyde, it is converted into secondary tetrahydro-α-picoline (α-pipecoleïne),

$$CH_2 <^{CH=\!=\!CH}_{CH_2\cdot CHMe} > NH,$$
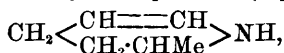
which is also formed by distillation of the aldehyde with potash; it boils at 123·5—125·5° under a pressure of 750 mm. and is probably identical with the compound obtained by Ladenburg by the action of bromine on α-pipecoline. The hydrochloride crystallises in colourless needles melting at 204°. The picrate is oily.

In addition to amidocaproaldehyde, the oxidation of α-pipecoline gives rise to a ketonic or aldehyde acid in small quantity; it is contained in the residue after the steam distillation of the aldehyde. It crystallises from a mixture of alcohol and acetone in stellate groups of colourless needles, melts at 103·5°, and has one or other of the formulæ $CHO\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$;

$$NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot COOH.$$
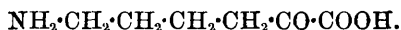
With hydrogen peroxide in excess, α-pipecoline yields formic, acetic, and succinic acids. Coniïne and β-pipecoline closely resemble α-pipecoline in their behaviour towards hydrogen peroxide, α-picoline is much more stable, and even after a considerable time only yields small quantities of formic acid. These results, as well as the numerous syntheses of pyridine derivatives which are known show how close the connection is between this class of compounds and the members of the fatty series, and render it easier to understand the formation of pyridine compounds (alkaloïds) by plants.   J. B. T.

Synthesis of Hydroquinoline Derivatives. By I. GUARESCHI (*Chem. Centr.*, 1893, ii, 454; from *Atti Accad. Sci. Torino*, 1893).— Ethylic cyanacetate readily acts on orthamidoacetophenone forming a substance which crystallises in silky needles, melts at 330—332°, and has the composition $C_{11}H_8N_2O$. It is *β-cyano-α-methylpseudo-carbostyril*, or *β-cyanolepidone*, $C_6H_4 <^{CMe\vdots C\cdot CN}_{NH\cdot CO}$;   in its formation

the two compounds unite with elimination of alcohol, the cyanorthamidoacetophenone thus obtained undergoing intra-molecular condensation with loss of water. β-Cyanolepidone is almost insoluble in water, sparingly soluble in alcohol, and with silver salts yields the *silver* compound $C_{11}N_2H_7OAg$. On distillation with zinc dust, it is converted into lepidine, thus confirming the formula already given.

If orthamidobenzaldehyde is substituted for the acetophenone derivative, the corresponding *cyanopseudocarbostyril*, or β-*cyano-α-ketodihydroquinoline*, $C_6H_4\!<^{CH:C\cdot CN}_{NH\cdot CO}$, is obtained; this crystallises in long needles or lustrous, yellowish plates, melts at 329—331° with decomposition, and yields a *silver* compound $C_{10}H_5N_2OAg$.

H. G. C.

Pyrazolidone. By R. v. ROTHENBURG (*Ber.*, **26**, 2972—2975). —Hydrazine hydrate acts on acrylic acid with formation of pyrazolidone, $CO\!<^{NH\cdot NH}_{CH_2\cdot CH_2}$; this boils at 132—135°, has a sharp, pyrazolone-like smell, and is insoluble in alkalis, but soluble in acids. Ferric chloride converts it by oxidation into pyrazolone, and nitrous acid into isonitrosopyrazolone (Abstr., 1893, i, 611). It instantly reduces ammoniacal silver solution.

Phenylhydrazine reacts in a similar manner with acrylic acid, 1-phenylpyrazolidone, $CO\!<^{NPh\cdot NH}_{CH_2-CH_2}$, being produced. This substance separates from benzene in crystals melting at 119—121°, and boils at 299—301°. It has been previously prepared by the action of phenylhydrazine on the β-halogen-propionic acids (C. F. Böhringer Söhne, German Patent, 53834). It behaves towards reagents in the same manner as pyrazolidone, being converted by oxidation into 1-phenylpyrazolone (*Ber.*, **24**, 433c), and by nitrous acid into *isonitroso*-1-*phenylpyrazolone*, $CO\!<^{NPh-\!\!-\!\!-N}_{C(NOH)\cdot CH}$, the silver salt of which is a reddish-yellow, granular powder.

A. H.

Action of Halogens on 1-Phenylpyrazole. By O. SEVERINI (*Real. Accad. Linc.*, 1892, ii, 391—394; compare Abstr., 1893, i, 671).— Chlorine acts on 1-phenylpyrazole suspended in water, either with or without the addition of potash, yielding 1-phenylchloropyrazole, melting at 74·5—75·5°, which the author has previously prepared by the action of sodium hypochlorite on phenylpyrazole.

The 1-phenyldibromopyrazole, melting at 84°, is obtained on adding bromine to 1-phenylpyrazole suspended in dilute potash (1 per cent.). Iodine has no action on 1-phenylpyrazole at 100° under ordinary conditions; a solution of iodine in potassium iodide acts on the pyrazole in potash solution, with formation of 1-*phenyliodopyrazole*, $C_9H_7IN_3$. This substance is volatile in a current of steam, and crystallises in small, white needles melting at 76·5°; it is soluble in alcohol and in ether.

W. J. P.

Synthesis of Compounds containing Carbon-Nitrogen Rings from Orthoamidobenzylamine and its Derivatives. By M. BUSCH (*Chem. Centr.*, 1893, ii, 578—584; from *Hab. Schrift. Erlangen*). —The substituted amidobenzylamines are prepared by the reduction of the corresponding nitro-compounds with zinc dust and acetic acid at a low temperature. The derivatives containing an aliphatic alkyl group are liquid and strongly basic in character, whilst the derivatives of the aromatic series are crystalline and less basic, but give stable salts with acids.

Orthamidobenzylamine, $NH_2 \cdot C_nH_4 \cdot CH_2 \cdot NH_2$, is a liquid. *Orthamidobenzylmethylamine*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NHMe$, is an almost colourless oil, which has a bitter taste and alkaline reaction, and is readily soluble in water. *Orthamidobenzylethylamine* is a yellowish oil. *Orthamidodibenzylamine* is an almost colourless oil, slightly soluble in water, readily in alcohol, &c. *Orthamidobenzylparanisidine*,

$$NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot OMe,$$

crystallises in yellowish-white, lustrous scales melting at 82°. *Orthamidobenzylparaphenetidine*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot OEt$, crystallises in white, nacreous plates melting at 78°. *Orthamidobenzylparachloraniline*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4Cl$, crystallises in white, lustrous needles melting at 89—90°. *Orthamidobenzylparabromaniline* forms white needles melting at 104°. *Orthamidobenzyl-α-naphthylamine* crystallises in almost white, lustrous plates, with a faint tinge of red, and melts at 134°; its solutions show a bluish-red fluorescence. *Orthamidobenzyl-β-naphthylamine* forms white, lustrous plates melting at 99°; its solutions have a bluish-violet fluorescence. Many of the salts of the above compounds are also described by the author, together with the corresponding nitro-compounds and other derivatives.

Orthamidobenzylamine itself condenses with aldehydes to form the corresponding tetrahydroquinazolines, $C_6H_4 \big\langle {}^{NH \cdot CHX}_{CH_2 \cdot NH}$. The substitution products of the base, on the other hand, form benzylidene compounds of the type $RHN \cdot CH_2 \cdot C_6H_4 \cdot N:CHX$. The latter are decomposed by dilute mineral acids into their components. When treated with metallic sodium in alcoholic solution, the benzylidene compounds take up 2 atoms of hydrogen, and are converted into the substitution derivatives of the corresponding base,

$$RHN \cdot CH_2 \cdot C_6H_4 \cdot NH \cdot CH_2X.$$

With the exception of orthamidobenzylparachloraniline and the corresponding bromine derivative, these substances yield di-acid derivatives of the carboxylic acids.

The condensation products of the bases described above with benzaldehyde, salicylaldehyde, formaldehyde, and paranitrobenzaldehyde and their derivatives are also described in the paper.

The nitrobenzylamines, when heated on the water bath with benzenesulphonic chloride, are converted into nitrobenzylaminephenylsulphones of the type $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot N(SO_2Ph)R$, and these, on reduc-

tion, yield the corresponding amido-bases, but are not converted into anhydro-compounds.

The orthamidobenzylamines react with carbonyl chloride and with carbon bisulphide to form keto- and thio-derivatives of tetrahydroquinazoline, $C_6H_4{<}^{NH \cdot CO}_{CH_2 \cdot NR}$ and $C_6H_4{<}^{NH \cdot CS}_{CH_2 \cdot NR}$. The compounds thus obtained are not identical with those prepared by Söderbaum and Widmann from the corresponding carbamide and thiocarbamide derivatives of orthamidobenzylic alcohol, although, from the method of formation, substances of identical constitution would be expected. The thiotetrahydroquinazolines are converted by the action of freshly precipitated mercuric oxide at 150° into the keto-derivatives. When treated with energetic reducing agents, the thio-derivatives are converted into tetrahydroquinazolines. Both the keto- and thio-compounds are oxidised by permanganate to the same diketo-derivatives, $C_6H_4{<}^{NH \cdot CO}_{CO \cdot NR}$. With the exception of the derivatives prepared from orthamidobenzylamine itself, these keto- and thio-compounds are completely indifferent to acids and bases. Methylic iodide forms the hydriodide of the corresponding methyl derivative, and the compound thus produced has strongly marked basic characters.

Ketotetrahydroquinazoline, $C_8N_2H_8O$, forms either a white, amorphous mass, or indistinct, white, microscopic needles melting at 180°. It is soluble in alcohol and acetic acid, but almost insoluble in water. *Phenylketotetrahydroquinazoline*, $C_8N_2H_7PhO$, crystallises from ethylic acetate in transparent, four-sided plates with an adamantine lustre, and from alcohol, on dilution with water in broad, pointed needles or thick plates. It softens at 186°, and melts at 189°. *Paratolylketotetrahydroquinazoline* crystallises from alcohol in lustrous needles and from ethylic acetate in transparent prisms melting at 218—220° ; it is readily soluble in boiling alcohol, but insoluble in water. *Phenetylketotetrahydroquinazoline* forms fascicular groups of colourless needles melting at 223°. *Parabromophenyltetrahydroquinazoline* crystallises in transparent, quadratic plates melting at 226°.

Thiotetrahydroquinazoline, $C_8N_2H_8S$, is prepared by heating orthamidobenzylamine with an excess of carbon bisulphide and an equal volume of dilute alcoholic potash ; it forms white, lustrous plates melting at 210—212°. *Ethylthiotetrahydroquinazoline* crystallises in white, lustrous plates, melts at 185°, and is very soluble in benzene and chloroform. *Phenylthiotetrahydroquinazoline* forms colourless needles, or large transparent plates, slightly soluble in alcohol, more readily in boiling acetic acid. It softens and becomes yellow at 235°, and melts at about 245°. *Paratolylthiotetrahydroquinazoline* crystallises in white, flat needles, softens at 230°, and melts at 235°. *Phenetylthiotetrahydroquinazoline* separates in white, silky needles melting at 238°. *Parachlorophenylthiotetrahydroquinazoline* forms lustrous, silver-white plates, melts at 228°, and is soluble in carbon bisulphide and boiling acetic acid. *Parabromothiotetrahydroquinazoline* crystallises from absolute alcohol in transparent, four-sided prisms melting at 234°. *α-Naphthylthiotetrahydroquinazoline* crystallises from amyl

alcohol in transparent, lustrous plates melting at 255°.   *β-Naphthyl-thiotetrahydroquinazoline* forms brilliant, transparent plates, melts at 280°, and is soluble in acetic acid.

Tetrahydroquinazoline, $C_6H_4 \big\langle {}^{NH \cdot CH_2}_{CH_2 \cdot NH}$, crystallises in white plates.

which are soluble in water, and melts at 81°.   *α-Naphthyltetrahydro-quinazoline* forms white, lustrous plates, readily soluble in absolute alcohol, &c., and melts at 134°.   *β-Naphthyltetrahydroquinazoline* forms yellowish plates melting at 135—139°.

When the substituted orthamidobenzylamines are treated with nitrous acid, the diazo-compounds which are first produced are immediately converted, with elimination of the elements of hydrogen chloride, into phenodihydrotriazines of the type $C_6H_4 \big\langle {}^{N \,=\, N}_{CH_2 \cdot NR}$. Thus β-phenophenyldihydrotriazine may be prepared by the action of nitrous acid on orthamidobenzylaniline, and it is also obtained when orthamidobenzylphenylhydrazine is treated with nitrous acid, the nitrosamine of orthamidobenzylaniline, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NPh \cdot NO$, being probably formed as an intermediate product.

β-Phenophenyldihydrotriazine forms lustrous, yellowish plates, and melts at 128° with evolution of gas.   *β-Phenomethyldihydrotriazine* separates from boiling light petroleum in yellowish plates, and from ethylic acetate in large, lustrous crystals melting at 72—73°.   *β-Phen-ethyldihydrotriazine* is a yellow oil, and forms salts which crystallise well.   *β-Phenobenzyldihydrotriazine* is precipitated in snow-white needles, on adding water to its alcoholic solution and crystallises in large, six-sided tablets, melting at 91° with evolution of gas.   *β-Pheno-paratolyldihydrotriazine* crystallises from alcohol in yellow, lustrous, rhomboidal plates, and from ether in thick crystals with an adamantine lustre, and melts at 151°.   *β-Phenoparanisyldihydrotriazine* forms lustrous, crystalline scales, and melts with decomposition at 139°. *β-Phenoparaphenetyldihydrotriazine* crystallises in golden-yellow, lustrous plates, melting at 144° with evolution of gas.   *β-Phenoparachloro-phenyldihydrotriazine* separates from hot alcohol in golden plates, and from benzene in thick, transparent crystals melting at 134°.   *β-Pheno-parabromophenyldihydrotriazine* forms pale yellow, lustrous plates, melting at 164°.   *β-Phenacetyldihydrotriazine* separates from alcohol at 60° in lustrous plates, and from ether in flesh-coloured, rhomboidal plates; it softens at 136°, and melts at 138° with evolution of gas.   *β-Phenobenzoyldihydrotriazine* forms white, lustrous needles melting at 114—115° with evolution of nitrogen.

The β-phenodihydrotriazines are basic compounds, and, with the exception of those containing acid radicles, which are only slightly basic, give stable salts.   They are themselves very unstable, melt with evolution of nitrogen, and show a remarkable similarity to the diazo-compounds.   In aqueous solution, the salts decompose on heating with evolution of nitrogen and formation of the corresponding hydr-oxybenzylamine, whilst heating with a concentrated halogen acid leads to the formation of the corresponding halogen derivative.   With amines and phenols, they yield the deeply-coloured azo-compounds

which are characteristic of the diazo-compounds. Thus with β-naphthol, the product is of the type $OH \cdot C_{10}H_6 \cdot N_2 \cdot C_6H_4 \cdot CH_2 \cdot NHR$. These colouring matters are acted on by reducing agents in the usual manner. Gentle oxidising agents have, as a rule, no action on the triazines, whilst stronger reagents cause a breaking up of the molecule. On reduction, the phenodihydrotriazines are converted into the corresponding amidobenzylamine, ammonia being eliminated. When β-phenotolyldihydrotriazine is heated at its melting point, nitrogen is evolved, and benzylidenetoluidine, $CHPh:N \cdot C_7H_7$, is left as an oil.

When the orthonitrobenzylnitrosamines are reduced, the corresponding amidobenzylhydrazines are formed.

Orthonitrobenzylphenylnitrosamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NPh \cdot NO$, separates from alcohol in coarse, yellow crystals, and from ether in clear, vitreous prisms melting at 84°. *Orthamidobenzylphenylhydrazine*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NPh \cdot NH_2$, crystallises in vitreous needles melting at 102°. *Orthonitrobenzylparatolylnitrosamine* forms lustrous, yellow needles melting at 80°. *Orthamidobenzylparatolylhydrazine* crystallises in snow-white, lustrous needles melting at 66°. *Orthonitrobenzylparaphenetylnitrosamine* forms orange-coloured plates melting at 95°. *Orthamidobenzylparaphenetylhydrazine* crystallises in colourless needles or rhomboidal tablets melting at 98°. *Orthonitrobenzylparachlorophenylnitrosamine* crystallises in yellow, transparent prisms melting at 100°. *Orthamidobenzylparachlorophenylhydrazine* forms transparent prisms melting at 95°. *Orthonitrobenzylparabromophenylnitrosamine* crystallises in microscopic plates melting at 107°. *Orthamidobenzylparabromophenylhydrazine* forms lustrous tablets melting at 119—120°. *Orthonitrobenzyl-β-naphthylnitrosamine* crystallises in dark yellow plates melting at 102°. *Orthamidobenzyl-β-naphthylhydrazine* forms small needles melting at 76°.

The amidobenzylhydrazines are powerful bases. They reduce Fehling's solution and silver oxide at the ordinary temperature, form very hygroscopic salts with the mineral acids, and condense with aldehydes to form dibenzylidene compounds.

The amidobenzylhydrazines react with carbonyl chloride and carbon bisulphide in a manner similar to the amidobenzylamines, yielding products of the type

$$C_6H_4 \begin{subarray}{l} < \end{subarray} \begin{smallmatrix} NH \cdot CO \\ CH_2 \cdot NR \end{smallmatrix} > NH \text{ and } C_6H_4 < \begin{smallmatrix} NH \cdot CS \\ CH_2 \cdot NR \end{smallmatrix} > NH.$$
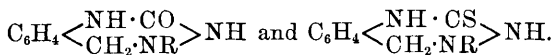
These substances melt between 250° and 300° with evolution of gas and decomposition, and are much less stable than the corresponding quinazoline derivatives, into which they tend to pass. The thiocarbamides derived from the amidobenzylhydrazines, for example, when treated with metallic sodium in alcoholic solution, yield the corresponding tetrahydroquinazolines, ammonia and hydrogen sulphide being evolved. These seven-ring compounds are indifferent towards both acids and alkalis.　　　　　　　　　　　　　　　　　　　A. H.

Action of Cyanogen on Hydrazine. By A. ANGELI (*Gazzetta,* **23**, ii, 103—104).—On passing a rapid current of cyanogen into an

aqueous solution of hydrazine, and strongly cooling, a *substance* of the composition $C_2N_6H_8$ separates; it forms large prisms which do not melt at 230°. It readily acts on aldehydes and ketones, and may therefore have the constitution $C(NH \cdot NH_2)_2(NH)_2$. When treated with nitrous acid, it gives a white, crystalline product; this is probably the *ditetrazole*, $\overset{N-N}{\underset{N \cdot NH}{||}} \!\!> C \cdot C \!<\!\! \overset{N-N}{\underset{NH \cdot N}{||}}$.   W. J. P.

Sparteïne. By F. B. AHRENS (*Ber.*, **26**, 3035—3042; compare Abstr., 1893, i, 232) —The author has already described the formation of trioxysparteïne by the action of hydrogen peroxide on oxysparteïne. If oxysparteïne hydrochloride is treated with dilute hydrogen peroxide, no trioxysparteïne is obtained, but a quantitative yield of a *new base*, $C_{15}H_{24}N_4O_2$, which crystallises from ether in white needles. The *hydrochloride*, $C_{15}H_{24}N_4O_2,HCl$, crystallises, with $3\frac{1}{2}H_2O$, in white needles. The *dihydrochloride*, $C_{15}H_{24}N_2O_2,2HCl + 3\frac{1}{2}H_2O$, crystallises in transparent prisms. The *hydrobromide*, $C_{15}H_{24}N_2O_2,HBr + 4H_2O$, forms transparent crystals. The *platinochloride*,

$$(C_{15}H_{24}N_2O_2)_2,H_2PtCl_6 + 6H_2O,$$

crystallises in orange leaflets or needles, and decomposes at 236°. The *aurochloride* crystallises in lustrous leaflets, darkens at 186°, and melts at 194° with decomposition.

A *base* of the composition $C_{15}H_{26}N_2O$ is obtained by boiling sparteïne with freshly prepared silver oxide or mercuric oxide and water. It is an oil which quickly darkens on exposure to air. The *hydriodide*, $C_{15}H_{26}N_2O,HI$, crystallises in leaflets, and melts at 211°. The *platinochloride* forms small, sparingly soluble crystals, and melts at 108°. The *aurochloride* forms microscopic crystals, and melts at 175° with decomposition.

A *base* isomeric with the preceding is obtained by boiling sparteïne with freshly prepared lead peroxide and water. It is a hygroscopic resin, easily soluble in water. The *platinochloride* forms small crystals, darkens at 230°, and decomposes at 256°. The *aurochloride* is a crystalline powder, and melts at 178—180° with decomposition.

Dehydrosparteïne, $C_{15}H_{24}N_2$, is obtained by shaking sparteïne with a concentrated solution of bleaching powder. It is a liquid closely resembling sparteïne, and boils at 314—316° (uncorr.) without decomposition. The *hydrochloride*, $C_{15}H_{24}N_2,2HCl + 2\frac{1}{2}H_2O$, forms large, colourless crystals resembling ammonium chloride, and carbonises at 270°. The *hydrobromide* crystallises with $1H_2O$. The *hydriodide*, with $1H_2O$, melts at 258°. The *platinochloride*, with $2H_2O$, crystallises in beautiful, indented plates, and melts at 237° with decomposition. The *aurochloride* crystallises in sparingly soluble needles, gradually blackens when heated, and froths up at 168°.

Sparteïne sulphate, when distilled under 16—20 mm. pressure with zinc-dust and zinc oxide, yields a mixture of bases, namely, diethylmethylamine, pyridine, α-picoline, a base which was not identified. 2:3:6-trimethylpyridine, sparteïne, and a *base* of the formula $C_{10}H_8N_2$, which melts at 94—101°, and yields an *aurochloride* melting at 190° with decomposition.   E. C. R.

Meconinemethyl Methyl Ketone and Di-meconinemethyl Ketone. By F. HEMMELMAYR (*Monatsh.*, **14**, 390—399).—Meconinemethyl methyl ketone, $\begin{smallmatrix} CO-\!\!-\!\!-\!\!-O \\ C_6H_2(OMe)_2 \end{smallmatrix}\!\!>\!CH\cdot CH_2\cdot COMe$ (Abstr., 1892, 179), is hydrolysed by boiling baryta water partly into the hydroxy-acid by severance of the lactone bond, and partly into opianic acid and acetone. When, however, a mixture of opianic acid and acetone is boiled with baryta water, condensation occurs, and meconinemethyl methyl ketone is formed. The ketone is hydrolysed by alkaline permanganate also into opianic acid and acetone, the latter substance being of course further oxidised to formic acid. The hydrolysis is not due to the action of the alkali. The *phenylhydrazone* is described; it melts at 159—160°. Meconinemethyl methyl ketone is converted by boiling bromine water into a *monobromo-derivative*.

Di-meconinemethyl ketone, $CO[CH_2\cdot CH\!<\!\begin{smallmatrix} C_6H_2(OMe)_2 \\ O \end{smallmatrix}\!\!>\!CO]_2$ (*loc. cit.*), is hydrolysed by boiling baryta water in the same way as the mono-compound.

The author claims priority in the preparation of a phenylhydrazine-lactone additive compound, namely, the dihydrazone of meconinemethyl phenyl ketone (Abstr., 1893, i, 181). JN. W.

Action of Methylic Iodide on Papaverinic acid. By F. SCHRANZHOFER (*Monatsh.*, **14**, 597).—The author finds that the normal barium salt of the methylbetaïne of papaverinic acid, $C_{34}H_{28}N_2O_{14}Ba$ (this vol., i, 59), crystallises with $6H_2O$.

G. T. M.

Cinchonine. By M. FREUND and W. ROSENSTEIN (*Annalen*, **277**, 277—290).—A preliminary account of the author's experiments has already been published (Abstr., 1892, 892).

The specific rotatory power of dimethylcinchonine dihydrochloride, that is, of the basic hydrochloride (*loc. cit*), dissolved in dilute hydrochloric acid is $[\alpha]_D = +5\cdot37°$ at 20°. When to the last-mentioned solution platinic chloride is added, a *platinochloride*,

$$C_{21}H_{26}N_2O,H_2PtCl_6 + 2H_2O,$$
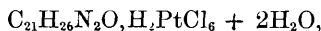
is precipitated. The hydrobromide, $C_{21}H_{26}N_2O,HBr$, melts at 118—120° (not 111°; *loc. cit.*). The *picrate*, $C_{21}H_{26}N_2O,2C_6H_3N_3O_7$, melts at 160°; the *zincochloride*, $C_{21}H_{26}N_2O,HZnCl_3$, melts at 220°; and the *mercurochloride* at 222°. *Dimethylcinchonine ethiodide* melts at 138°; *dimethylcinchonine benzylic chloride* was prepared.

Methylcinchonine, dimethylcinchonine, methylcinchonine methosulphate, and dimethylcinchonine methosulphate all yield cinchoninic acid when oxidised by Skraup's method (*Annalen*, **201**, 291); this fact shows that the alkyl groups are combined with one and the same nucleus.

When dimethylcinchonine methiodide is boiled with concentrated alkali, it decomposes into trimethylamine, and a *base* which yields a yellow, amorphous *platinochloride*, $(C_{19}H_{19}NO)_2,H_2PtCl_6$, that does not melt at 280°.

The presence of a quinoline nucleus explains how the nitrogen atom in one-half of the molecule of cinchonine is combined, whereas the function of the second nitrogen atom is still obscure.

<div style="text-align: right">A. R. L.</div>

Pseudocinchonine. By E. LIPPMANN and F. FLEISSNER (*Monatsh.*, **14**, 371—375).—When cinchonine trihydriodide is heated with water ($\frac{1}{2}$ to $\frac{3}{4}$ vol.) for 5—6 hours at 150—160°, it gradually dissolves, and, on keeping the solution, a yellow, acicular precipitate gradually falls, consisting of the hydriodide of pseudocinchonine, a base isomeric with cinchonine.

The base may be isolated by means of the sparingly soluble normal sulphate. The product of the above action is precipitated with ammonia, and the mixed bases suspended in water and cautiously neutralised with dilute sulphuric acid. Pseudocinchonine sulphate soon separates, whilst the sulphates of cinchonine and iso-cinchonine remain in solution. The free base is precipitated by ammonia from the hot aqueous solution.

Pseudocinchonine, $C_{19}H_{22}N_2O$, is a white, flocculent or granular substance melting at 214—216° (cinchonine melts at 250—252°, and iso-cinchonine at 126—127°). It is soluble in ether, and may be thus readily separated from cinchonine. The *normal sulphate* forms long, slender, asbestos-like needles, and, unlike the corresponding salts of cinchonine and its other isomerides, is anhydrous. The *platino-chloride* and *dihydriodide* are described.

<div style="text-align: right">JN. W.</div>

Chitenine. By R. v. BUCHER (*Monatsh.*, **14**, 598—611).—When chitenine, the oxidation product of quinine, is heated for two hours with $2\frac{1}{2}$ times its weight of benzoic chloride, the *benzoyl derivative*, $C_{19}H_{21}N_2O_4Bz$, is obtained. It is readily soluble in alcohol, ether, and benzene, and is precipitated by light petroleum from its benzene solution in the form of a pale yellow powder, which melts at 85°. The *platinochloride*, $C_{19}H_{21}N_2O_4Bz,H_2PtCl_6$, is a bright yellow, crystalline powder. The *platinochloride*, $C_{19}H_{19}N_2O_4Ac_3,H_2PtCl_6 + 3H_2O$, obtained from the *acetyl derivative* of chitenine is also a microcrystalline powder.

On passing hydrogen chloride through a cooled solution of chitenine in absolute alcohol, the *ethyl derivative*, $C_{19}H_{21}N_2O_4Et$, is obtained; it crystallises in needles, melts at 198°, and unites with ethylic iodide to form the compound $C_{19}H_{21}N_2O_4Et,EtI$, which crystallises from alcohol in slender, white prisms, and melts at 210°.

Chitenol, $C_{18}H_{20}N_2O_4 + H_2O$, is obtained on heating chitenine with 10 times its weight of colourless hydriodic acid for three hours at 100°. It crystallises from hot water, in which it is only sparingly soluble, in slender, white needles; dissolves readily in acids and alkalis, decomposes at 270°, without previously melting, gives the quinine reaction with chlorine water and excess of ammonia, and yields the following salts :—The *sulphate*, $C_{18}H_{20}N_2O_4,H_2SO_4 + H_2O$, is fairly soluble in water, and crystallises in slender, bright yellow scales; the *hydrochloride*, $C_{18}H_{20}N_2O_4.2HCl + H_2O$, crystallises in plates, and the *platinochloride*, $(C_{18}H_{20}N_2O_4),2HCl,H_2PtCl_6$, in yellow

prisms. On oxidising chitenol with alkaline permanganate, products are formed from which two calcium salts can be obtained. Of these, one is insoluble, and contains per cent., C, 35·69 ; H, 2·36 ; Ca, 16·59. The other is readily soluble and contains per cent., C, 40·04—42·25 ; H, 2·65—4·10; Ca, 12·36—13·83 ; N, 5·43. G. T. M.

Alkaloïds of Belladonna. By O. HESSE (*Annalen*, **277**, 290—300 ; compare Abstr., 1891, 748 ; 1892, 1498).—Merck (Abstr., 1892, 1255) stated that atropamine was identical with Pesci's apoatropine (Abstr., 1882, 740) ; he has since shown (Abstr., 1893, i, 491) that the latter alkaloïd, like atropamine, may be converted into belladonnine.

Apoatropine could not be prepared by following Pesci's directions, but is obtained without secondary products when a solution of atropine sulphate in nitric acid of sp. gr. 1·381 is kept at the ordinary temperature for 24 hours ; or when atropine sulphate or hyoscyamine sulphate is dissolved in concentrated sulphuric acid in the cold, and the solution poured into water ; or when the last-named salts are heated at 85° with acetic, benzoic, or phosphoric anhydride ; but not when they are treated under any circumstances with hydrochloric acid. The base is difficult to obtain in a crystalline condition, and the author now confirms Merck's observations (*loc. cit.*), that it is identical with atropamine.

Belladonnine is obtained when a solution of atropine or of hyoscyamine in concentrated sulphuric acid is allowed to remain for a short time. The platinochloride melts at 229°, and the aurochloride at 120°. If hyoscyamine is slowly raised to a temperature of 120—130°, it is first converted into atropine, thence into apoatropine, and finally into belladonnine. When apoatropine is treated with alkalis or with hydrochloric acid, it is converted either into belladonnine or decomposition products of the latter, or undergoes more advanced decomposition ; the reason therefore that both Pesci and Merck obtained tropine from apoatropine was, that they subjected the alkaloïd to too violent treatment with alkalis, and thus precluded the formation of belladonnine.

When apoatropine is heated in a sealed tube with fuming hydrochloric acid (8 parts) for eight hours at 85—100°, belladonnine and tropine are formed ; if, however, the solution is heated for 16 hours at 140°, bellatropine is obtained. The platinochloride, $C_8H_{15}NO_2,H_2PtCl_6$, melts at 212°, and the aurochloride at 163°. The base crystallises in colourless prisms. A. R. L.

Hyoscine. By O. HESSE (*Annalen*, **277**, 304—308; compare Abstr., 1893, i, 679).—The author brings forward fresh evidence in support of the following views. Ladenburg's hyoscine is identical with scopolamine ; it has the composition represented by the formula $C_{17}H_{21}NO_4$, and on decomposition at 60—100° yields oscine, $C_8H_{13}NO_2$, which is identical with scopoline. Scopolamine (hyoscine) hydrobromide is therefore not a new mydriatic. A. R. L.

Melting Point of Cocaïne Hydrochloride. By O. HESSE (*Annalen*, **277**, 308—309; compare Abstr., 1893, i, 679).—When cocaïne hydrochloride is heated at 160—161° in a Roth's apparatus, it sinters at the end of 15 minutes, swells up after 25 minutes, and is completely fused in 31 minutes; these changes take place, although more slowly, even at as low a temperature as 152—154°.

A. R. L.

Alkaloïds from the Rind of Pomegranate Root. By G. CIAMICIAN and P. SILBER (*Ber.*, **26**, 2738—2753; compare Abstr., 1893, i, 287).—Pseudopelletierine appears to be a ketoamine ; it does not contain hydroxyl or methoxyl, and is probably a higher homologue of tropine, which it closely resembles. Their experimental results are insufficient to enable the authors to suggest a constitutional formula for the base ; they propose the term *granatonine* in place of pseudopelletierine, so as to bring the nomenclature of the derivatives into uniformity with those of tropine.

The production of *granatoline*, $C_9H_{17}NO$, from granatonine (pseudopelletierine) has been previously described (*loc. cit.*) ; the reduction is more readily accomplished by means of sodium and alcohol than by sodium amalgam and water ; it forms feathery, colourless crystals, melts at 100°, boils at 251° under 761 mm. pressure, and does not combine with hydroxylamine. The yield is theoretical. The *hydrochloride* is hygroscopic. The aurochloride melts at 213° with previous softening, not at 203°. The *methiodide*, $C_9H_{15}NO,MeI$, crystallises in colourless cubes melting at 307° ; on distilling it with potash, the base is regenerated. The *benzoyl derivative* was analysed in the form of its *platinochloride*, $(C_9H_{16}NOBz)_2,H_2PtCl_6$, which is yellow and crystalline.

Granatenine, $C_9H_{15}N$, is prepared by the action of hydriodic acid and phosphorus on granatoline; it is a viscid liquid of somewhat unpleasant odour, and boils at 186° under a pressure of 751 mm. The *aurochloride*, $C_9H_{15}N,HAuCl_4$, is obtained in stellate crystals melting at 220° with decomposition. The *methiodide*, $C_9H_{15}N,MeI$, crystallises in cubes which are not melted at 315°. On distillation with potash, the methiodide undergoes a similar decomposition to that of tropidine methiodide with formation of *methylgranatenine*, $C_9H_{14}NMe$; this closely resembles β-methyltropidine, and boils at 210—220°. The *aurochloride*, *picrate*, and *methiodide* are crystalline and unstable.

Granataldehyde, $C_8H_{12}O$, the analogue of tropilen, is formed, together with dimethylamine, by heating the preceding base in hydrochloric acid solution ; it is a mobile, readily soluble liquid, with an aromatic odour, boils at 200—201° under 758 mm. pressure, and readily reduces ammoniacal silver solution. The *phenylhydrazone* is an oily, unstable liquid ; an additive compound is formed with hydrogen sodium sulphite, but could not be isolated. The *dibromide*, $C_8H_{12}OBr_2$, is formed at 0°, and crystallises from light petroleum in colourless needles melting at 100°.

Granatyl iodide, $C_9H_{16}NI,HI$, is occasionally obtained as a bye-product in the preparation of granatenine (see above), but the exact conditions necessary for its formation remain undetermined. It is

deposited from water in colourless, feathery crystals melting at 200° with decomposition, blackens on exposure to light, and is readily converted into granatenine on treatment with alkalis.

By the action of hydriodic acid and phosphorus on granatenine or granatoline at 240° for 8—12 hours, two bases are formed; the one is termed granatanine, the other, which corresponds to "norhydrotropidine," is called norgranatanine. *Granatanine*, $C_9H_{17}N$, is a camphor-like substance with an odour resembling that of coniine; it melts at 49—50°, boils at 192—193° under 763 mm. pressure, is readily soluble in water, and has a strongly alkaline reaction. The *aurochloride*, $C_9H_{17}N,HAuCl_4$, crystallises in feathery, pale yellow needles melting at 229°. *Norgranatanine*, $C_8H_{15}N$, was obtained in small quantity, and separated from the preceding base by means of its crystalline *carbamate*. The *aurochloride* is deposited in yellow plates which melt at 225°.   J. B. T.

Ipecacuanha. By B. H. PAUL and A. J. COWNLEY (*Pharm. J. Trans.*, **53**, 61—63).—The so-called "emetine" is a mixture of at least two different alkaloïds, the greater part being an amorphous substance, of marked alkalinity, and forming definite neutral salts, which are also amorphous, and cannot be obtained crystalline by any means yet tried. The amorphous alkaloid is associated with others that are distinctly crystalline, and much less soluble in ether, chloroform, or benzene. In the stem of Brazilian ipecacuanha, a crystalline alkaloïd is present in a larger proportion, relatively to the amorphous alkaloïd, than in the root. The authors are seeking means of separating the alkaloïds with the view of determining their several amounts and their chemical and therapeutic properties. They find that the quantity of the mixed alkaloïds obtainable from different samples of ipecacuanha root does not vary much from 2 per cent.   R. R.

Alkaloïds of Pereiro Bark. By O. HESSE (*Annalen*, **277**, 300—302).—The author found (*Annalen*, **202**, 141) that pereiro bark contained, besides geissospermine and pereirine, another alkaloïd which appears to be identical with that described by Freund and Fauvet (Abstr., 1893, i, 446) under the name of geissospermine. It differs from the author's geissospermine in having a higher melting point (189°). Both dissolve in nitric acid with a purple-red colour, but the coloration produced by Freund and Fauvet's base is more persistent. The same remarks apply to the behaviour of the two compounds with an acid solution of molybdic sulphate; the colourless solution of Freund and Fauvet's base becomes intensely purple-red when heated. Geissospermine hydrochloride is amorphous, but the hydrochloride of the other base is crystalline; other differences are recorded.   A. R. L.

Nucleïc Acid. By L. LIEBERMANN and B. v. BITTÓ (*Chem. Centr.*, 1893, ii, 649; from *Centr. Med. Wiss.*, 1893, 465—467).—The nucleïc acid prepared from beer yeast by Altmann's method may be shown by the test proposed by Liebermann to contain metaphosphoric acid.

The analysis of the baryta precipitate gave, after subtraction of the organic matter, Ba 48·87, PO₃ 51·12 per cent. Although the composition calculated for $Ba(PO_3)_2$ is Ba 46·44, and PO₃ 53·56 per cent., the authors believe that the relation of Ba to PO₃ can only correspond with barium metaphosphate. Kossel has also come to hold the view which he formerly opposed, that the phosphoric acid in nucleïc acid is present in the form of metaphosphoric acid. It is not necessary to submit nucleïc acid to a prolonged digestion, or to any severe treatment, in order to obtain xanthine substances.   A. H.

Thymin; a Decomposition Product of Nucleïc acids. By A. KOSSEL and A. NEUMANN (*Ber.*, **26**, 2753—2756).—The nucleïc acids, of which at least four appear to exist, are compounds of an acid with various bases, such as adenine, hypoxanthine, guanine, and xanthine. The nucleïc acid prepared from the thyroid gland of calves yields adenine on boiling with water, and is therefore termed adenylic acid. In addition to the adenine, two acids are formed : both are soluble in dilute hydrochloric acid ; the one combines directly with albumin to form an insoluble compound, and is, perhaps, the nucleïc acid corresponding to paranucleïn. The second acid is termed *thymic acid*, it does not precipitate albumin, and, on heating with sulphuric acid (30 per cent.), *thymin*, $C_{23}H_{26}N_8O_6$, is formed. This substance has neither basic nor acidic properties ; it decolorises bromine water, sublimes without decomposition, melts above 250°, and is deposited from water in quadratic and hexagonal crystals. Thymin is also obtained in small quantity by heating adenylic acid. The authors differ from L. Liebermann, who regards the nucleïns as compounds of albumin with metaphosphoric acid ; they consider that this view is disproved by the production of thymin.   J. B. T.

Glucoside Constitution of Proteïd Matter. By F. W. PAVY (*Proc. Roy. Soc.*, **54**, 54—57).—By the action of potash on proteïd matter (purified coagulated egg albumin), the author has obtained a product which forms a hard, glassy mass when dry, gives readily a clear solution with water, yields no coloration with iodine, and does not reduce Fehling's solution. It is precipitated by absolute alcohol, and closely resembles Landwehr's " animal gum." By the action of mineral acids, it is converted into a substance which reduces Fehling's solution ; this substance presents the appearance of a sugary extractive, and has a pronounced baked sugar odour. It is very soluble in water, but only slightly so in absolute alcohol ; it is readily diffusible, and dissolves cupric hydroxide in presence of excess of potash without producing a biuret reaction. Heated on the water bath for 2 to 3 hours with phenylhydrazine and acetic acid, it gives a crystalline osazone, and has the characteristics of a sugar. It seems to be optically inactive, or possibly very slightly lævorotatory.

    J. W.

Organic Chemistry.

Cryoscopic Behaviour of Substances of Similar Constitution to the Solvent. By F. GARELLI (*Gazzetta*, **23**, ii, 354—382).— Ferratini and Garelli (Abstr., 1893, 156; 512) have already studied numerous cases of abnormal depression of the freezing points of various solvents produced by a number of substances; the cause of this anomalous behaviour was found in the similarity of constitution which exists between the solvent and the substance in such cases, which leads to the formation of solid solutions (compare Van Bijlert, Abstr., 1891, 1411).

Quinoline and isoquinoline give much too high values for the molecular weight in naphthalene solution, although the former base exercises the normal depression on the freezing point of benzene. Acridine gives too high a molecular weight in phenanthrene solution, the depression is normal, however, in benzene and in naphthalene; the author supposes that a solid solution of acridine in phenanthrene is formed. Pyrroline and tetrahydroquinoline give very high values in naphthalene solution; dihydronaphthalene also gives abnormal values, as would be expected from the fact that this substance is isomorphous with naphthalene. Tetrahydrodiphenyl and a-tetrahydronaphthol also behave abnormally if diphenyl and a-naphthol respectively are used as solvents. Tetrahydrocarbazole gives the normal molecular weight in naphthalene, but alters the freezing point of phenanthrene very slightly, this constant being raised if changed at all. Carbazole gives normal values in diphenylamine.

These facts indicate that the formation of solid solutions, and the consequent vitiation of the results of the molecular weight determinations, are conditioned not so much by similarity in the chemical behaviour of the substances concerned as by similarity in constitution. This view is supported by the normal depressions of the freezing points of phenol by pyrroline; these two substances are somewhat similar in respect to chemical behaviour but totally different in molecular configuration. A possible method is thus indicated for determining the constitution of organic substances. Although the constitution of nicotine is not as yet definitely settled, the old view that this base is hexahydrodipyridyl has been disproved by Pinner and by Blau (Abstr., 1893, i, 489; 736). This is confirmed by the observation that nicotine does not form solid solutions with diphenyl whilst γ-dipyridyl does; the constitution of nicotine should, consequently, not be of the same type as that of dipyridyl.

The high values obtained for the molecular weight of phenol by the boiling point method in benzene are usually attributed to the formation of solid solutions; it is much more likely, however, that the abnormal rise in the boiling point is due to the general tendency of hydroxy-compounds to condense. Very high molecular weights are obtained for resorcinol in benzene and naphthalene solutions, operating by the cryoscopic and boiling point methods respectively.

Chlorobenzene, bromobenzene, and benzonitrile depress the freezing point of benzene almost normally. β-chloronaphthalene and the α- and β-naphthylamines give high results in freezing naphthalene; α-nitronaphthalene, however, depresses the freezing point normally. Benzidene gives the normal molecular weight in phenol.

The solid solutions obtained in the above experiments being only isomorphous mixtures, the constituents of such mixtures should have approximately the same crystalline form. The close relation existing in this respect between phenanthrene and anthracene and between the two naphthols and naphthalene is at once evident from crystallographic data respecting these substances furnished by Negri.

<div align="right">W. J. P.</div>

Nitromethane and its Homologues. By BERTHELOT and MATIGNON (*Ann. Chim. Phys.*, [6], **30**, 565—572).—Nitro derivatives are formed from the hydrocarbons of the paraffin series and nitric acid with the development of heat, which is comparable to that observed in the case of nitrobenzene; the high values of their heats of formation explain the stability and fundamental difference between the reactions of the nitro compounds as compared with those of the ethereal nitrites.

Nitromethane :—Heat of combustion at constant volume $+ 170\cdot25$ cal., and at constant pressure $+ 169\cdot8$ cal. Specific heat (between $23°$ and $80°) = 0\cdot471$. Heat of volatilisation, $6\cdot98$ Cal. Heat of formation (calculated), from elements C diamond $+ H_3 + N + O_2 = CH_3\cdot NO_2$ liquid $+ 28\cdot8$ Cal.; or $CH_3\cdot NO_2$ gas $+ 21\cdot8$ Cal. Heat of formation from methane and nitric acid CH_4 gas $+ HNO_3$ liquid $= H_2O$ liquid $+ CH_3\cdot NO_2$ liquid $+ 36\cdot7$ Cal.; or $CH_3\cdot NO_2$ gas $+ 29\cdot17$ Cal. It is thus seen that the heat of formation of nitromethane is a little less than that of nitrobenzene. Heat of dissolution $- 0\cdot60$ Cal. Heat of neutralisation $+ 7\cdot01$ Cal. (potassium hydroxide); and $+ 8\cdot9$ Cal. (barium hydroxide).

Nitroethane :—Heat of combustion at constant volume $+ 322\cdot45$ Cal., and at constant pressure $+ 322\cdot30$ Cal. Specific heat $0\cdot451$ (between $23°$ and $95°$). Heat of volatilisation $+ 6\cdot90$ Cal. Heat of formation (calculated) from its elements $+ 38\cdot8$ Cal. for the liquid, $+ 31\cdot8$ Cal. for the gaseous compound; from ethane and nitric acid $+ 43\cdot0$ cal. for the liquid, and $+ 36\cdot0$ Cal. for the gaseous compound. Heat of neutralisation (potassium hydroxide) $+ 10\cdot1$ Cal.

<div align="right">A. R. L.</div>

Hexamethylene Dibromide. By W. H. PERKIN, JUN. (*Ber.*, **27**, 216—217).—A preliminary notice, published in consequence of the appearance of a paper by Salonina on the same subject (this vol., i, 119). By acting on trimethylene chlorobromide, C_3H_6ClBr, with an alcoholic solution of sodium ethoxide, *chloropropylic ethylic ether*, $C_3H_6Cl\cdot OEt$, is obtained as a colourless oil, boiling at $132—134°$. Metallic sodium condenses it into *hexamethyleneglycol diethylic ether*, $C_3H_6(OEt)_2$, an oil which was not analysed, but was converted by strong hydrobromic acid at $150°$ into *hexamethylene dibromide*, $C_6H_{12}Br_2$, an oil boiling at $135—137°$ under 20 mm. pressure. This, in xylene solution, is condensed by finely-divided metallic sodium to hexamethylene,

$CH_2 <^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}> CH_2$, boiling at 77—80°, previously obtained by Baeyer (this vol., i, 174). C. F. B.

Action of Nitric acid on Nononaphthene. By M. KONOVALOFF (*J. Russ. Chem. Soc.*, **25**, 389—429).—When nononaphthene, C_9H_{18}, is heated with nitric acid, it is partially converted into a mononitro-derivative, the yield of which varies greatly with the concentration of the acid, temperature, &c. The author obtained the most favourable results by heating 4 c.c. of the hydrocarbon with 20 c.c. of nitric acid (sp. gr. 1·075) for five hours at 130°. About half of the hydrocarbon is attacked under these conditions, and of this portion 40—50 per cent. is converted into the crude nitro-derivative. A larger yield may be obtained by using a weaker acid or a lower temperature, but the action then proceeds very slowly; on the other hand, boiling in open vessels with strong acid does not give favourable results.

From the crude nitro-product two fractions were obtained, one boiling under 40 mm. pressure at 126—129° (sp. gr. at 20°/0° = 0·9797), and the other at 130—132° (sp. gr. at 20°/0° = 0·9908). Both have the composition $C_9H_{17} \cdot NO_2$, both attack sodium in benzene, are themselves partially dissolved by concentrated potash, and form a pseudonitrole with nitrous acid. The mononitrononaphthene is therefore not homogeneous, but consists of a mixture of a secondary and a tertiary nitro-product. The crude nitro-product gives 20 per cent. of the secondary derivative soluble in potash, and 62 per cent. of the tertiary derivative insoluble in potash.

On reduction with zinc and acetic acid, the higher boiling fraction yielded, besides an amine, a ketone of the formula $C_9H_{16}O$. The *amine*, $C_9H_{17} \cdot NH_2$, distils mostly at 173—175°, and consists of two isomeric compounds which may be partially separated by crystallisation of their platinochlorides.

The *secondary nitrononaphthene*, $C_9H_{17} \cdot NO_2$, is an almost colourless oil boiling at 224—226°, and does not solidify in a freezing mixture. Its sp. gr. at 20°/0° is 0·9903, and at 0°/0° 1·0043. Its molecular refraction, calculated by means of Lorenz's formula, is 47·40. When bromine is added in excess to its clear solution in caustic potash, the *monobromo-derivative*, $C_9H_{16}Br \cdot NO_2$, is formed; this is a heavy, colourless oil, sp. gr. at 0°/0° = 1·3330, and at 20°/0° = 1·3112, molecular refraction 54·51. On reduction, secondary nitrononaphthene gives the *secondary amidononaphthene*, $C_9H_{17} \cdot NH_2$, boiling at 175·5—177·5°, having the sp. gr. 0·8434 at 0°/0°, 0·8273 at 20°/0°, and the molecular refraction 45·62. The chloride, sulphate, and nitrate do not crystallise, but the picrate and platinochloride are crystalline.

Tertiary nitrononaphthene, $C_9H_{17} \cdot NO_2$, boils with some decomposition at 220—225°, and has the sp. gr. 0·9919 at 0°/0°, its molecular refraction being 47·41. It gives Liebermann's reaction, but neither a nitrole nor pseudonitrole. On reduction, it yields the *tertiary amidononaphthene*, $C_9H_{17} \cdot NH_2$, boiling at 173—175°, and having a sp. gr. of 0·8485 at 0°/0°, and the molecular refraction 45·32. It is slightly

soluble in water. The chloride may be crystallised from light petroleum.

The neutral product obtained on the reduction of the crude nitro-derivative was proved to be a *ketone* having the composition $C_9H_{16}O$, and boiling at 180—182°. It is a colourless, mobile liquid of sp. gr. 0·8903 at 0°/0°. Its *oxime* boils with decomposition at 220—225°, and seems to consist of a mixture of different substances, as a small quantity of the ketone re-obtained from it boiled at 168—172°.

<div align="right">J. W.</div>

α-Decanaphthene. By ZUBKOFF (*J. Russ. Chem. Soc.*, **25**, 382—385).—The fraction of Caucasian petroleum boiling between 160° and 172° consists chiefly of decanaphthenes. The portion boiling at 160—162° (α-decanaphthene), when chlorinated, gives rise to the compounds $C_{10}H_{19}Cl$, $C_{10}H_{18}Cl_2$, and $C_{10}H_{17}Cl_3$.

The dichloro-derivative, when heated with quinoline, yields a hydrocarbon, $C_{10}H_{16}$, which boils between 162° and 170°, and shows the reactions of a terpene.

The monochloro-derivative (b. p. 206—209°) can be converted into an acetate which boils at 224—230°, and into an alcohol, $C_{10}H_{19}\cdot OH$, which boils at about 215°.

A naphthylene, $C_{10}H_{18}$ (b. p. 159—162°), is formed at the same time as the acetate when the monochloride is heated at 210° with sodium acetate and acetic acid.

<div align="right">J. W.</div>

Suberone. By V. MARKOVNIKOFF (*J. Russ. Chem. Soc.*, **25**, 364—378).—Suberone (10 grams) is dissolved in absolute alcohol, and to the boiling solution sodium (20 grams) is gradually added. The alcohol is subsequently distilled off and the residue treated with water, when an oil separates; a further quantity of this can be extracted from the aqueous solution by treatment with ether. This oil is a monhydric alcohol, $C_7H_{13}\cdot OH$, which the author calls *suberylic alcohol* or *suberol*. It boils at 184—185° under 755 mm. pressure, and its sp. gr. at 15°/15° is 0·9595. The chloride obtained from it by the action of phosphorus pentachloride boils at 173—175°, is lighter than water at the ordinary temperature, and has the sp. gr. 1·0133 at 0°/0°. The urethane, $NHPh\cdot CO\cdot OC_7H_{13}$, melts at 85°, is insoluble in water, but easily soluble in alcohol and in ether.

To obtain *suberoxime*, suberone (50 grams) and hydroxylamine hydrochloride (35 grams) are dissolved in 80 per cent. alcohol, dry powdered soda (40 grams) is then added, and the mixture boiled for 5—7 hours on the water bath. The oxime is liquid at the ordinary temperature, and boils at 230° (751 mm.); on cooling, it solidifies to a mass of crystals which melt at 23°; its sp. gr. at 20°/20° is 1·0228. It is insoluble in water, but attracts moisture from the air, and becomes liquid. The hydrochloride can be obtained in the form of small, colourless prisms.

Suberylamine, $C_7H_{13}\cdot NH_2$, may be obtained from suberoxime by reduction either with sodium in alcoholic solution or with sodium amalgam in alkaline aqueous solution. It is a colourless liquid with a mixed odour of ammonia and hydrocarbons. It boils at 169° (corr.), and only partially mixes with water. The hydrochloride is

obtained as a hygroscopic, crystalline mass, very soluble in water and alcohol, but only slightly so in ether. J. W.

Trehalose. By E. Winterstein (*Ber.*, **26**, 3094—3098).—The author has again investigated the products of the hydrolysis of trehalose, but has been unable to find any other product than glucose. The hydrolysis was effected by heating it with 5 per cent. sulphuric acid for six hours, and the solution, after the removal of sulphuric acid and concentration, fractionally precipitated by alcohol in four stages. The four fractions show all the properties of glucose, and give no evidence of the presence of other hexoses or pentoses. The rotatory power of the first and fourth fractions is lower than that of glucose, but this appears to be due to the presence of a bye-product. Previous investigators have sometimes obtained products having a higher specific rotatory power than glucose, but this was probably due to the presence of unaltered trehalose.

The molecular weight of trehalose, as determined by both Raoult's and Beckmann's methods, agrees with the formula $C_{12}H_{22}O_{11}$. It does not combine with phenylhydrazine, and, therefore, in the combination of the two glucose molecules both aldehyde groups must have undergone alteration. H. G. C.

Desiccation of Starch. By Bloch (*Compt. rend.*, **118**, 146—149). —Starch does not lose the whole of its water, even after many hours' heating at 115°, and a temperature of 155—160° is required in order to expel the last traces. At this temperature, there is little or no conversion into dextrin if the starch is pure, but, even if such conversion took place, it would not affect the estimation of the water. C. H. B.

Starch. By C. J. Lintner (*Ber.*, **27**, 293—296).—In reply to the criticism of Scheibler and Mittelmeier (this vol., i, 107), the author explains the grounds which led him to an independent examination and discussion of the amyloïn theory proposed by Brown and Morris. A. H.

New Carbohydrate from Boletus Edulis. By E. Winterstein (*Ber.*, **26**, 3098—3099).—The fungus *Boletus edulis* contains, in addition to trehalose, a carbohydrate, which may be isolated by warming with sulphuric acid the residue left after the removal of fats and proteïds. The jelly thus obtained is boiled with water, the solution filtered, the filtrate concentrated, and precipitated with alcohol. The carbohydrate is freed from sulphuric acid by treatment with dilute alcohol, and then forms a pale yellow, amorphous mass, which gradually dissolves in 5 per cent. aqueous potash. It is slowly inverted by boiling dilute sulphuric acid, and is coloured yellow by iodine in presence of zinc chloride or concentrated sulphuric acid. Its optical properties could not be ascertained, as it forms opalescent solutions. The author proposes for it the name *paradextran*.

The analysis agrees fairly well with the formula $C_6H_{10}O_5$, and the only product of hydrolysis whose presence could be ascertained was glucose. H. G. C.

Methylenamidoacetonitrile. By R. JAY and T. CURTIUS (*Ber.*, **27**, 59—62).—*Methylenamidoacetonitrile*, $CH_2:N\cdot CH_2\cdot CN$, is obtained by adding formaldehyde to a strong solution of potassium cyanide and ammonium chloride and allowing the mixture to remain. It crystallises in lustrous, colourless prisms, melts at $129\cdot5°$, decomposes when boiled, and is easily soluble in dilute mineral acids, but is quickly decomposed in acid solution into formaldehyde and amidoacetonitrile. When boiled with alcoholic hydrochloric acid in a reflux apparatus, it yields ethylic amidoacetate hydrochloride,
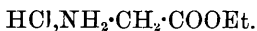
$$HCl,NH_2\cdot CH_2\cdot COOEt.$$

Amidoacetonitrile hydrochloride, $HCl,NH_2\cdot CH_2\cdot CN$, is obtained by treating the preceding compound with alcoholic hydrochloric acid at the ordinary temperature. It crystallises in lustrous tablets, is very hygroscopic, and, when warmed with dilute acid, is quickly converted into glycocine hydrochloride and ammonium chloride. *Amidoacetonitrile* is obtained by shaking the hydrochloride with silver oxide. It is a pale yellow oil, having a characteristic odour, and decomposes when distilled, even in a vacuum. When dissolved in acetic acid and treated with sodium nitrite, it yields a compound which the authors believe to be *diazoacetonitrile*, $N_2:CH\cdot CN$. This is a golden-yellow oil, has an odour resembling that of cyanogen, partially decomposes when distilled in a vacuum, and, when reduced with sodium hydroxide and ferrous sulphate, yields hydrazine sulphate.   E. C. R.

Behaviour of Unsaturated Bases towards Hydrogen Chloride. By W. JACOBI and G. MERLING (*Annalen*, **278**, 1—20).—Merling showed (Abstr., 1891, 1506) that certain unsaturated bases were converted by hydrogen chloride into pyrrolidine bases; in the present paper, the authors describe the similar transformation of analogous bases.

Dimethyl-β-pipecolinammonium iodide, $CH_2{<}^{CH_2-CH_2}_{CHMe\cdot CH_2}{>}NMe_2I$, crystallises from alcohol in stout, well-formed prisms, melts at $196-197°$, and, when treated with moist silver chloride, yields the *chloride*, which is a deliquescent, crystalline mass. The *platinochloride* melts at $258-259°$, and the *aurochloride* at $235-236°$. When dimethyl-β-pipecolinammonium chloride is distilled, methylic chloride and *methyl-β-pipecoline*, $CH_2{<}^{CH_2-CH_2}_{CHMe\cdot CH_2}{>}NMe$, pass over; the latter is an oil immiscible with water, having the odour of piperidine, boils at $124-126°$, and has a sp. gr. $= 0\cdot818$ at $15°$. The *platinochloride* melts at $156-158°$.

Methylbutallylcarbindimethylamine,

$$CH_2:CH\cdot CH_2\cdot CHMe\cdot CH_2\cdot NMe_2,$$

is prepared by digesting dimethyl-β-pipecolinammonium iodide with moist silver oxide and distilling the resulting hydroxide; it is a colourless oil, having the odour of piperidine, is not miscible with water, boils at $129-130°$ and has a sp. gr. $= 0\cdot767$ at $15°$. When

the fused hydrochloride is treated with hydrogen chloride, *hydro-chloromethylbutallylcarbindimethylamine hydrochloride*,

$$CHMeCl\cdot CH_2\cdot CHMe\cdot CH_2\cdot NMe_2, HCl,$$

is formed; the *platinochloride* melts at 77—78°, and the *aurochloride* at 68—70°. If an aqueous solution of the last-named hydrochloride is treated with sodium hydroxide at 0°, a mixture of the *hydrochloro-base* and methylbutallylcarbindimethylamine is produced; the latter is driven over with steam, and the residual alkaline solution is neutralised with hydrochloric acid and evaporated to dryness. Alcohol extracts from this mass *dimethyl-αβ-dimethylpyrrolidinammonium chloride*, $\begin{matrix} CHMe\cdot CH_2 \\ CH_2\cdot CHMe \end{matrix}>NMe_2Cl$; and this, on dry distillation, yields methylic chloride and *methyl-αβ-dimethylpyrrolidine*, $\begin{matrix} CHMe\cdot CH_2 \\ CH_2\cdot CHMe \end{matrix}>NMe$, which is a colourless oil having the odour of piperidine; it boils at 111—113°, and its sp. gr. = 0·790 at 15°. The *platinochloride* melts at 179—180°, and the *aurochloride* at 98—99°.

Methylallylacetone, $C_3H_5\cdot CHMe\cdot COMe$, is prepared from ethylic methylallylacetoacetate; it is a colourless liquid, having a pleasant odour, boils at 138—140°, and has a sp. gr. = 0·845 at 15°. The *phenylhydrazone* is a yellow oil, and, when reduced with sodium amalgam in warm glacial acetic acid solution, yields *methylbutallyl-methylcarbinamine*, $C_3H_5\cdot CHMe\cdot CHMe\cdot NH_2$, which is a colourless oil immiscible with water; it has the odour of piperidine, boils at 133—136°, and its sp. gr. = 0·793 at 15°. The *platinochloride* melts with decomposition at 157—158°. The *hydrochloro-base*,

$$CHClMe\cdot CH_2\cdot CHMe\cdot CHMe\cdot NH_2,$$

forms a *platinochloride*, melting at 157—158° with decomposition, and, when heated, it is converted into *ααβ-trimethylpyrrolidine hydrochloride*, $\begin{matrix} CHMe\cdot CHMe \\ CH_2 — CHMe \end{matrix}>NH, HCl$. The *base* is volatile with steam; it is a colourless oil miscible with water, has the odour of piperidine, boils at 126—128°, and its sp. gr. = 0·816 at 15°. The *platinochloride* melts at 205—206° with decomposition.

Allylbutallylmethylcarbinamine, $CH(C_3H_5)_2\cdot CHMe\cdot NH_2$, is prepared by the reduction of diallylacetonephenylhydrazone; it is a colourless oil not miscible with water, has the odour of piperidine, boils at 174—176°, and its sp. gr. = 0·826 at 15°. The *platinochloride* melts at 159—160° with decomposition. The *hydrochloro base*,

$$CHClMe\cdot CH_2\cdot CH(C_3H_5)\cdot CHMe\cdot NH_2,$$
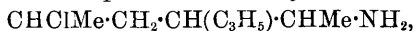
is a colourless oil, having a penetrating, unpleasant odour; it forms a *platinochloride*, melting with decomposition at 158—159°. If an ethereal solution of the hydrochloro base is heated, *αα-dimethyl-β-allylpyrrolidine hydrochloride*, $\begin{matrix} CH(C_3H_5)\cdot CHMe \\ CH_2——CHMe \end{matrix}>NH, HCl$, is obtained. The *base* boils at 174—176°, and its sp. gr. = 0·685 at 15°; the *platinochloride* forms orange-yellow plates.   A. R. L.

Compounds of Hexamethylenamine with Hydrogen Bismuthoiodide. By H. LEY (*Annalen*, **278**, 57—60).—Kraut has shown (*Annalen*, **210**, 310) that compounds are obtained from amines and hydrogen bismuthoiodide.

Hexamethylenamine hydriodide is precipitated when absolute alcohol is added to mixed concentrated aqueous solutions of hexamethylenamine and hydriodic acid ; it separates from aqueous alcohol in large crystals, and melts at 170—171°.

The *compound* $3(C_6H_{12}N_4,HI),BiI_3$ (A), separates as an orange, amorphous precipitate when a 20 per cent. solution of hexamethylenamine is stirred into a cold 5 per cent. solution of potassium bismuthoiodide ; the crude precipitate is washed with absolute alcohol, and dried over concentrated sulphuric acid. The same compound is obtained when potassium bismuthoiodide is added to an alcoholic solution of hexamethylenamine hydriodide ; the presence of water tends towards the production of compounds richer in bismuth. If the precipitate is allowed to remain in contact with an excess of potassium bismuthoiodide, it becomes olive-green, but, on being washed with alcohol, again changes to orange ; it consists of the compound $2(C_6H_{12}N_4,HI),BiI_3$. When the freshly-precipitated compound (A) is heated with alcoholic hydriodic acid, a portion dissolves, and six-sided plates, having the same composition, are precipitated from the filtrate ; the portion remaining undissolved also becomes crystalline, and consists of the compound $2(C_6H_{12}N_4,HI),BiI_3$. If the freshly-precipitated compound (A) is warmed with excess of potassium bismuthoiodide, purple microscopic, six-sided plates of the *compound* $C_6H_{12}N_4,HI,BiI_3$ are obtained.

The stability and characteristic properties of these derivatives render them suitable for the detection of hexamethylenamine.

A. R. L.

Ring Formation in Organic Nitrogen Compounds. By A. MICHAEL (*J. pr. Chem*, [2], **49**, 26—43).—By adding ethylic carbonate to a solution of sodium and guanidine thiocyanate in alcohol and neutralising the liquid after some days, ethylic guanidinedicarboxylate (guanidine diethylcarbonate ; Nencki, this Journal, 1875, 754) is precipitated. The filtrate contains guanoline $CN_3H_4·COOEt$ (*loc. cit.*). When ethylic oxalate is substituted for the carbonate, oxalylguanidine (Traube, this vol., i, 7) is formed, and this is also the product of the action of ethylic oxalate on guanidine itself, but when guanidine carbonate is used, a considerable quantity of *guanidine-ethylic oxalate*, $COOEt·COO·NH_2:C(NH_2)_2$, may be obtained. This crystallises in cubes, and melts at 134—136° when quickly heated, solidifying again at 165°, when it becomes hydrated oxalylguanidine ; it dissolves freely in water, but only sparingly in organic solvents. The reaction between thiocarbamide, sodium ethoxide, and ethylic oxalate produces thioparabanic acid.

Guanidine thiocyanate, sodium ethoxide, and ethylic malonate interact to form malonylguanidine (Traube, *loc. cit.*). When guanidine reacts with ethylic malonate, *guanidine-ethylic malonate* is produced ; it crystallises in prisms. With guanidine carbonate, malonylguanidine is formed. The action of ethylic sodiomalonate

on thiocarbamide gives rise to the sodium derivative of thiobarbituric acid.

A *compound*, $C_7O_3N_3H_{13}$, whose constitution has not been settled, is prepared by mixing sodium ethoxide, guanidine thiocyanate, and ethylic succinate in alcohol; it crystallises in white, prismatic needles, melts with decomposition at 190—191°, and is freely soluble in hot water. Another *compound*, $C_{11}H_{23}N_9O_6$, is obtained by the action of guanidine on ethylic succinate; it forms small prisms which do not melt at 300°, and is decomposed by hydrochloric acid with formation of the *compound* $C_5H_9N_3O_3$, which crystallises in needles, melts at 184—185°, and dissolves in hot water. When guanidine carbonate is used, *guanidine-ethylic succinate*, $COOEt \cdot CH_2 \cdot CH_2 \cdot COO \cdot NH_3 \cdot CN_2H_3$, is formed; this crystallises in prisms, melts at 136—138°, and is very soluble in water.

The mixture of guanidine thiocyanate and sodium ethoxide, used in the above cases, may be applied to the synthesis of many guanidine derivatives; in this way there have been obtained, with phenylisocyanate, *diphenylcarbaminylguanidine*, $NH:C(NH \cdot CO \cdot NHPh)_2$ (m. p. 174—175°); with phthalic anhydride, the *derivative*,

$$COOH \cdot C_6H_4 \cdot CO \cdot NH \cdot CN_2H_3,$$
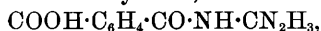
(m. p. 202—203°); with benzile, the *derivative*, $COPh \cdot CPh:N \cdot CN_2H_3$, (m. p. above 300°).   A. G. B.

Semicarbazide. By J. THIELE and O. STANGE (*Ber.*, **27**, 31—34). —Semicarbazide may be obtained from amidoguanidine or by the action of potassium cyanate on hydrazine sulphate (Abstr., 1892, 1295), and may be isolated in the form of the sparingly soluble compound with benzaldehyde. Benzalsemicarbazide, $NH_2 \cdot CO \cdot NH \cdot N:CHPh$, is best prepared by treating hydrazine sulphate which has been neutralised with sodium carbonate, with a slight excess of potassium cyanate, and leaving it over night. A small amount of hydrazodicarbonamide which separates is filtered off, and the filtrate shaken with benzaldehyde, the precipitate formed being then drained and washed with a little ether. The yield is nearly theoretical. *Acetone-semicarbazide*, $NH_2 \cdot CO \cdot NH \cdot N:CMe_2$, may be obtained in a similar manner by the action of acetone. It is tolerably soluble in cold water, less readily in alcohol, readily in acetone, and crystallises in needles, melting with decomposition at 186—187°. It is very easily decomposed by mineral acids.

Semicarbazide hydrochloride, $NH_2 \cdot CO \cdot NH \cdot NH_2, HCl$, is obtained by heating the benzaldehyde compound with fuming hydrochloric acid on the water bath, enough water being added to dissolve the whole mass. The benzaldehyde formed cannot be removed by distillation with steam, as the semicarbazide is thereby decomposed into carbonic anhydride, ammonia, and hydrazine; it must be extracted by shaking with benzene. The hydrochloride separates from a hot aqueous solution on cooling in small needles, and crystallises from alcohol in prisms, melting with decomposition at 173°. It is very soluble in water, less readily in strong hydrochloric acid, and insoluble in alcohol and ether. It is decomposed by continued boiling with acids or alkalis, and its alkaline solution has powerful reducing properties. Cupric chloride

produces a precipitate of a double salt, and platinum chloride is reduced even in acid solution. When the aqueous solution is boiled, a small amount of decomposition into hydrazodicarbonamide and hydrazine occurs. *Semicarbazide nitrate* is obtained by decomposing the acetone compound with nitric acid of sp. gr. 1·4. It is very soluble in water, from which it crystallises in prisms containing water, whilst it separates from alcohol in anhydrous crystals melting at 123° with decomposition. The *sulphate* may be prepared in a similar manner. On precipitating the hydrochloride with sodium picrate, *semicarbazide picrate* is obtained as a yellow mass, which is moderately soluble in water, and crystallises in needles. It melts at about 166°, after some previous decomposition.   A. H.

Hydrazides of Carbonic acid and of Thiocarbonic acid. By T. CURTIUS and K. HEIDENREICH (*Ber.*, **27**, 55—58).—*Carbamic hydrazide*: Semicarbazide, $NH_2 \cdot CO \cdot NH \cdot NH_2$, is obtained by heating a mixture of carbamide and hydrazine hydrate in molecular proportion for three hours in a sealed tube at 100°. It crystallises in colourless prisms, melts at 96°, and reduces Fehling's solution and ammoniacal silver solutions in the cold. When shaken with benzaldehyde it yields benzalsemicarbazide melting at 214°.

Semicarbazide nitrate, $NH_2 \cdot CO \cdot NH \cdot NH_2, HNO_3$, is obtained by evaporating semicarbazide with dilute nitric acid at 40°. It crystallises in lustrous tablets, and melts at 125° with evolution of gas. When diazotised, it yields *diazosemicarbazide nitrate*,

$$NH_2 \cdot CO \cdot NH \cdot N_2 \cdot NO_3 \text{ or } N_3 \cdot CO \cdot NH_2, HNO_3,$$
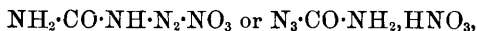
which crystallises in lustrous, colourless tablets, melts at 75—76°, yields nitrogen when boiled with dilute sulphuric acid, and does not yield azo-dyes. It probably has a constitution analogous to that of diazoguanidine nitrate as expressed by the second of the above formulæ.

Hydrazinedicarbonamide, $N_2H_2(CO \cdot NH_2)_2$, is obtained by heating the preceding compound (Abstr., 1893, i, 299). It is more easily obtained by heating carbamide (2 mols.) with hydrazine hydrate (1 mol.) at 130—150°. When oxidised with chromic acid, it yields azodicarbonamide, $N_2(CO \cdot NH_2)_2$.

Carbazide, $CO(NH \cdot NH_2)_2$, is obtained by heating ethereal salts of carbonic acid with hydrazine hydrate at 100°. It forms colourless crystals, melts at 152—153°, and combines with 2 mols. of benzaldehyde to form the compound $CO(NH \cdot N:CHPh)_2$, which melts at 198°.

Diammonium dithiocarbazate, $NH_2 \cdot NH \cdot CS \cdot SN_2H_5$, is obtained by the action of hydrazine hydrate on carbon bisulphide in the cold. It crystallises in white prisms, melts at 124° with decomposition, and decomposes with evolution of hydrogen sulphide in cold aqueous solution, more quickly when warmed. It gives insoluble precipitates with salts of the heavy metals. The *silver salt*, $NH_2 \cdot NH \cdot CSSAg$, is a bright yellow powder. The *lead salt* is a lemon-yellow powder.
                                                                    E. C. R.

Isosaccharic acid. By F. TIEMANN (*Ber.*, **27**, 118—138).—This acid, obtained from glucosamine or from the chitin of lobster shells,

by oxidation with nitric acid, has been reinvestigated, and found to be, not a tetrahydroxyadipic acid, but the anhydride of such an acid. It is not, however, a lactone, for it is still a bibasic acid ; probably it is a dihydroxytetrahydrofurfurandicarboxylic acid,

$$\left. \begin{array}{l} CH(OH) \cdot CH(COOH) \\ CH(OH) \cdot CH(COOH) \end{array} \right\rangle O.$$
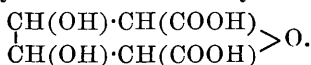
It, and several of its derivatives, readily unite with 1 mol. of water, yielding an acid, to which the name of *norisosaccharic acid* is given, or derivatives of this acid. These compounds, on their part, readily lose water and regenerate the original substances, and, on this ground, norisosaccharic acid might be regarded as merely a molecular compound of isosaccharic acid with water ; the author, however, prefers to regard it, at least provisionally, as a tetrahydroxyadipic acid,

$$COOH \cdot [CH(OH)]_4 \cdot COOH,$$
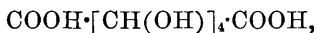
although it is not identical with either of the seven acids of this constitution already known. In preparing metallic salts, norisosaccharates are almost invariably obtained, but these at 100° readily lose their water of crystallisation, if they have any, and also another molecule of water, yielding isosaccharates. A solitary exception is furnished by lead isosaccharate, which can be obtained in anhydrous crystals by adding lead acetate to a hot solution of isosaccharic acid, and allowing the solution to cool. The molecular weight of several derivatives of isosaccharic acid was determined cryoscopically or ebullioscopically, and was found to agree with the above-mentioned view of the constitution of the acid. Further, isosaccharic acid and its calcium salt were found to exhibit birotation.

The following derivatives and salts were prepared. *Diethylic norisosaccharate,* white needles melting at 73°. *Diethylic isosaccharate,* melting at 101°. *Dimethylic norisosaccharate,* melting at 51°. *Diethylic tetracetylnorisosaccharate,* yellowish-white crystalline mass, melting at 47°, and readily losing acetic anhydride with formation of *diethylic diacetylisosaccharate,* which melts at 49°. *Diacetylnorisosaccharic acid,* white needles melting at 174° ; at 100° they lose water yielding *diacetylisosaccharic acid,* which also melts at 174°. The following formulæ represent the metallic norisosaccharates prepared ; at 100° they all lose water, and yield the corresponding isosaccharates. $C_6H_9O_8K + \frac{1}{2}H_2O$; $C_6H_8O_8K_2$. $C_6H_9O_8(NH_4)$; $C_6H_8O_8(NH_4)_2$. $C_6H_8O_8Ca + H_2O$. $C_6H_8O_8Sr + H_2O$. $C_6H_8O_8Ba + H_2O$. $C_6H_8O_8Cu + 3H_2O$. $C_6H_8O_8Pb + H_2O$. $C_6H_8O_8Zn + 3H_2O$. $C_6H_8O_8Mg + 2H_2O$. Isosaccharic acid itself forms crystals which melt at 185° ; norisosaccharic acid is only known in aqueous solution as a syrup which, when allowed to remain in a vacuum desiccator, slowly deposits crystals of isosaccharic acid. C. F. B.

Glucosamine. By E. FISCHER and F. TIEMANN (*Ber.,* **27,** 138— 147).—When glucosamine hydrochloride is treated with silver nitrite, a sugar, *chitose,* is formed. This has not yet been isolated, but has been converted by oxidation with bromine into the monobasic *chitonic acid,* which, on oxidation with nitric acid, yields a basic isosaccharic

acid. In a similar manner, bromine oxidises glucosamine hydro-bromide to *chitaminic acid*, and the hydrochloride of this, on treatment with silver nitrate, yields *chitaric acid*, which, when oxidised with nitric acid, yielded a quantity of an acid (? isosaccharic) too small to be identified. Heating with hydriodic acid and phosphorus reduces chitaminic acid to an acid, $C_6H_{13}NO_3$ (? amidohydroxycaproic), which melts with decomposition at 220—230°.

Chitonic acid was obtained as a colourless syrup by concentrating an aqueous solution; it is dextrorotatory, having, in a solution containing also calcium chloride and hydrochloric acid, $[\alpha]_D^{20} = +44\cdot5$. The *calcium salt*, $(C_6H_{11}O_7)_2Ca$, is also dextrorotatory, having $[\alpha]_D^{19} = +32\cdot8$. The other salts are amorphous.

Chitaminic acid, $C_6H_{13}NO_6$, forms colourless crystals, chars above 250°, and is feebly dextrorotatory. The *copper salt*, $(C_6H_{12}NO_6)_2Cu$, and the *hydrobromide*, $C_6H_{13}NO_6,HBr$, were analysed.

Chitaric acid appears to crystallise, but was not obtained in amount sufficient for purification; it is dextrorotatory. The *calcium salt*, $(C_6H_9O_6)_2Ca + 4H_2O$, forms colourless crystals.　　　C. F. B.

Polymeric Modifications of Aldehyde. By W. R. ORNDORFF and J. WHITE (*Amer. Chem. J.*, **16**, 43—69).—The authors have determined the molecular weight of metaldehyde, making use of Raoult's and Hoffmann's methods, and find that it is identical with that of paraldehyde, namely $(C_2H_4O)_3$. They suggest, therefore, that those two compounds must be represented by the same structural formula in a plane, but that the difference between them may be readily understood if they are regarded as stereo-isomerides; paraldehyde, the more stable modification, being the cistrans, whilst metaldehyde is the cis variety.

When metaldehyde is allowed to remain for a considerable time, the clear, tough, fibrous crystals, which are pulverised with difficulty, become brittle and opaque, and are converted into *tetraldehyde*, $(C_2H_4O)_4$, which is much more stable than metaldehyde, and is characterised by its greater solubility in phenol and thymol. Tetraldehyde closely resembles metaldehyde in its behaviour with reagents, and it may be reconverted into it by dissolving in warm chloroform and cooling the saturated solution in a freezing mixture.

　　　　　　　　　　　　　　　　　　　　G. T. M.

Amidoacetaldehyde III. By E. FISCHER (*Ber.*, **27**, 165—172). —The author has already described the preparation of the aldehyde from acetaltrimethylammonium hydroxide (Abstr., 1893, i, 300). Berlinerblau has also obtained the trimethylammonium derivative of the aldehyde by boiling the acetal compound obtained from trimethylamine and chloracetal with baryta. The author finds that the two compounds are identical. The aldehyde is not identical with muscarine, its physiological action being very different, and approaching that of choline. When oxidised with silver oxide, it is converted into betaïne, and the author therefore names it *betaïnaldehyde*. It is not decomposed by boiling with bases, and probably has the constitution

$$NMe_3 {<}{\overset{CH_2}{\underset{O-}{}}}{>} CH\cdot OH.$$
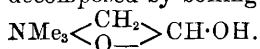
Benzoylacetalamine, when allowed to remain in contact with well-cooled, fuming sulphuric acid for a time, yields benzamide. A similar decomposition takes place when hippuric acid is heated with sulphuric acid at 100°.

A polymeride of amidoacetaldehyde, $C_4H_{10}N_2O_2$, is obtained by evaporating a mixture of acetalamine and hydrobromic acid to a syrup in a vacuum, and allowing the product to remain for some time over sulphuric acid. The *hydrobromide* so obtained crystallises in colourless, lustrous prisms. The *hydrochloride*, obtained by shaking the hydrobromide with silver chloride, separates in beautiful, colourless crystals. The *platinochloride*, $C_4H_{10}N_2O_2,H_2PtCl_6 + H_2O$, crystallises in beautiful, yellowish-red prisms or tablets, and decomposes at 200°. The *aurochloride* forms long yellow needles. The *free base*, obtained by shaking the hydrobromide with silver oxide, crystallises in beautiful, long, white needles or prisms, melts about 83°, is extremely hygroscopic, has a strongly alkaline reaction, and is not altered by boiling with alkalis and Fehling's solution. When warmed with concentrated sulphuric acid, it yields a solution which quickly reduces Fehling's solution, and shows all the reactions of the amidoaldehyde. The *dibenzoyl compound*, $C_{18}H_{18}N_2O_4$, crystallises in small needles, darkens at 200°, and melts at 230—250° with decomposition. E. C. R.

Hydrazidoacetaldehyde. By E. FISCHER and P. HUNSALZ (*Ber.*, **27**, 178—185).—*Hydrazidoacetal*, $NH_2 \cdot NH \cdot CH_2 \cdot CH(OEt)_2$, is obtained by heating hydrazine with absolute alcohol and chloracetal in an autoclave at 115—120° for six hours. It boils at 90—100° under 13 mm. pressure, has a characteristic ethereal odour, is strongly alkaline, and reduces Fehling's solution when gently warmed, and ammoniacal silver solution in the cold. The salts with mineral acids are very soluble in water and alcohol. The *picrate* separates in bright yellow crystals, and melts at 137—138°. The *acid oxalate* crystallises in slender, radiating needles, and melts at 136° with decomposition.

Hydrazidoacetal combines with benzaldehyde or nitrobenzaldehyde to yield oily hydrazones. With nitrous acid, it yields a pale yellow oil, and it also combines with methylic iodide, ethylic acetoacetate, and acetylcarboxylic acid. The *dibenzoylderivative*,

$$N_2HBz_2 \cdot CH_2 \cdot CH(OEt)_2,$$
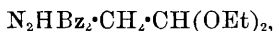
melts at 125°, is easily soluble in alkalis, does not reduce Fehling's solution, and reduces ammoniacal silver solution when heated. *Benzenesulphonehydrazidoacetal*, $SO_2Ph \cdot N_2H_2 \cdot CH_2 \cdot CH(OEt)_2$, obtained by shaking hydrazidoacetal with sodium hydroxide and benzenesulphonic chloride, melts at 68°, and slowly reduces Fehling's solution.

Oxalyldihydrazidoacetal, $C_2O_2[N_2H_2 \cdot CH_2 \cdot CH(OEt)_2]_2$, is obtained by adding ethylic oxalate to an aqueous solution of hydrazidoacetal. It melts at 134°, and reduces Fehling's solution when warmed.

Acetalylphenylthiosemicarbazide, $NHPh \cdot CS \cdot N_2H_2 \cdot CH_2 \cdot CH(OEt)_2$, is obtained by gradually adding phenylthiocarbimide to hydrazidoacetal. It crystallises in beautiful, large tablets, melts at 97—98°, and slowly reduces Fehling's solution when warmed. When heated with hydro-

chloric acid, it yields the *hydrochloride* of a *base* of the composition $C_{11}H_{15}N_3SO,HCl$, melting at 175° with decomposition.

Hydrazidoacetaldehyde hydrochloride, $COH \cdot CH_2 \cdot N_2H_3,HCl$, is obtained by gradually adding hydrazidoacetal to well cooled hydrochloric acid; it decomposes at 98° with violent evolution of gas, very easily reduces Fehling's solution, and yields ammonia when boiled with excess of alkali. The *free base* was not obtained. When the hydrochloride is treated with sodium acetate, an amorphous, yellow powder is obtained, which has the composition 37·24 per cent. C, 6·88 per cent. H, and 45·33 per cent. N. Glyoxalphenylosazone is obtained on warming the hydrochloide with phenylhydrazine.

E. C. R.

Carbamide Derivatives of Diacetonamine. By W. TRAUBE (*Ber.*, **27**, 277—280).—When a salt of diacetonamine is treated with potassium cyanate or thiocyanate, combination takes place, and substances are formed which are anhydrides of the corresponding carbamide derivatives. The constitution of these compounds is to be determined by further researches.

Anhydrodiacetonecarbamide, $C_7H_{12}N_2O$, is obtained by the action of potassium cyanate on diacetonamine oxalate. It crystallises from hot water or benzene in lustrous rhombohedra, melting at 194°.

Anhydrodiacetonethiocarbamide, $C_7H_{12}N_2S$, forms colourless needles, which are insoluble in water, readily soluble in alcohol, and melt at 249°, after becoming brown at a lower temperature.

Diacetonephenylthiocarbamide, $C_{13}H_{18}N_2SO$, is obtained by the direct combination of diacetonamine and phenylthiocarbimide. It forms lustrous plates, melts at 144°, and is slightly soluble in cold water, readily in alcohol. When hydrochloric acid is added to its boiling aqueous solution, the anhydro-compound is precipitated; this forms six-sided prisms, and melts at 191—192°. Like anhydrodiacetonethiocarbamide, it is insoluble in alkalis.   A. H.

Constitution of Stearolic acid. By J. BARUCH (*Ber.*, **27**, 172—176; see also Abstr., 1893, i, 551).—Stearolic acid,

$$C_8H_{17} \cdot C\dot{\colon}C \cdot [CH_2]_7 \cdot COOH,$$

when treated with concentrated sulphuric acid, yields ketostearic acid, $C_8H_{17} \cdot CO \cdot CH_2 \cdot [CH_2]_7 \cdot COOH$. The latter gives with hydroxylamine two stereoisomeric ketoximestearic acids, $\begin{array}{c} C_8H_{17} \cdot \underset{\parallel}{C} \cdot [CH_2]_8 \cdot COOH, \\ N \cdot OH \end{array}$ and $\begin{array}{c} C_8H_{17} \cdot \underset{\parallel}{C} \cdot [CH_2]_8 \cdot COOH. \\ HO \cdot N \end{array}$ When these are treated with concentrated sulphuric acid at 100°, the two acids, $C_8H_{17} \cdot NH \cdot CO \cdot [CH_2]_8 \cdot COOH$ and $C_8H_{17} \cdot CO \cdot NH \cdot [CH_2]_8 \cdot COOH$, are obtained, which, when heated with fuming hydrochloric acid at 180—200°, yield octylamine, $C_8H_{17} \cdot NH_2$, sebacic acid, $C_8H_{16}(COOH)_2$, pelargonic acid, $C_8H_{17} \cdot COOH$, and α-amidononanic acid, $NH_2 \cdot [CH_2]_8 \cdot COOH$. A detailed account of the isolation of these acids is given in the original paper.

Ketostearic acid crystallises in white, lustrous leaflets, and melts at 76°. The *ethylic* salt forms beautiful, lustrous, white leaflets, and melts at 41°.

The mixture of *ketoximestearic acids*, obtained by heating the preceding acid with hydroxylamine hydrochloride, sodium hydroxide, and alcohol on the water bath for two hours, forms a white, crystalline mass, stable towards alkalis, and decomposed by boiling with dilute acids into hydroxylamine and ketostearic acid. The mixture of the two acids obtained from them by the action of sulphuric acid melts at 70—80°. E. C. R.

Behenolic acid. By J. BARUCH (*Ber.*, **27**, 176—177).—The ethylic salt of the acid obtained by the action of sulphuric acid on behenolic acid has been analysed and gives numbers corresponding with the formula $C_3H_{17}\cdot CO\cdot[CH_2]_{12}\cdot COOEt$, thus confirming the author's previous results (Abstr., 1893, i, 551).

Ketobehenic acid, $C_8H_{17}\cdot CO\cdot[CH_2]_{12}\cdot COOH$, when treated in the manner described for stearolic acid in the preceding abstract, yields two stereoisomeric ketoximebehenic acids, and finally octylamine, dodecandicarboxylic acid, $COOH\cdot[CH_2]_{12}\cdot COOH$, pelargonic acid, and amidotriskaidecanic acid, $NH_2\cdot[CH_2]_{12}\cdot COOH$. E. C. R.

Halogen Derivatives of Ethylic Acetoacetate. By A. HANTZSCH (*Annalen*, **278**, 61—69).—An introduction to Epprecht's paper (next abstract).

Chloro- and Bromo- Derivatives of Ethylic Acetoacetate. By G. EPPRECHT (*Annalen*, **278**, 69—87).—The author disproves Haller and Held's observation that ethylic chloracetoacetate yields a mixture of α- and γ-cyanacetoacetates on treatment with potassium cyanide. He confirms Hantzsch and Schiffer's conclusion (Abstr., 1892, 697) that ethylic chloracetoacetate is the α-derivative. The chief product of the action between potassium cyanide and ethylic α-chloracetoacetate in ethereal solution is the *cyanhydrin*,

$$OH\cdot CMe(CN)\cdot CHCl\cdot COOEt,$$
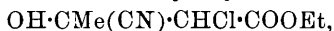
from which, however, neither citric acid nor ethylic acetonedicarboxylate are formed on hydrolysis. Ethylic α-chloracetoacetate reacts with potassium cyanide in alcoholic solution, forming the potassium derivative of ethylic α-cyanacetoacetate, and a small quantity of a *condensation* derivative, $C_{20}H_{26}N_2O_9$, which is insoluble in alkalis, and melts at 82°.

According to Nef (Abstr., 1892, 143), Duisberg's ethylic bromacetoacetate is a mixture of the α- and γ-derivatives; the author finds, however, in accordance with Hantzsch's observation, that it consists exclusively of the γ-derivative boiling at 125° (10 mm.); it is quantitatively converted into ethylic amidothiazylacetate (m. p. 94°) by means of thiocarbamide.

Schönbrodt's ethylic bromacetoacetate, obtained by brominating the copper derivative of ethylic acetoacetate, is the α-derivative; when treated with thiocarbamide, it is converted into ethylic amidomethylthiazolecarboxylate (m. p. 174°). When ethylic α-bromacetoacetate is treated with potassium cyanide, it yields the α-cyanoderivative (m. p. 26°); whilst ethylic γ-bromacetoacetate under similar treatment forms a compound which is, perhaps, the γ-cyano-

derivative, but which, on distillation in a vacuum, is decomposed into hydrogen cyanide and ethylic succinosuccinate.

Ethylic αγ-dibromacetoacetate, $CH_2Br\cdot CO\cdot CHBr\cdot COOEt$, is obtained by brominating ethylic γ-bromacetoacetate or its copper derivative; it forms white needles, and melts at 45—49°.

The *copper* derivative is a bright, yellowish-green precipitate which melts at 145°.

Ethylic αα-dibromacetoacetate, $COMe\cdot CBr_2\cdot COOEt$, obtained by brominating ethylic α-bromacetoacetate or its copper salt, is an oil; when treated with hydroxylamine, it is converted into Nussberger's ethylic methylsynglyoximecarboxylate (Abstr., 1892, 1175).   A. R. L.

Preparation of Suberic Acid. By V. MARKOVNIKOFF (*Ber.*, **26**, 3089—3092).—In this paper the author gives the details adopted in the preparation of suberic acid by the oxidation of cork and of castor oil with nitric acid; a yield of 5 per cent. was obtained from the former, and of 13 per cent. from the latter. When impure, suberic acid crystallises from water in indistinct aggregates, but when pure forms microscopic needles, and if allowed to crystallise slowly from a hot incompletely saturated aqueous solution, may be obtained in long, very slender needles, which fall to powder in the air. The pure compound melts at 140—141°.   H. G. C.

Additive Products of Ethylic Sodacetoacetate and Sodiomalonate with Ethereal Salts of Unsaturated Acids. By A. MICHAEL (*J. pr. Chem.* [2], **49**, 20—25; compare Abstr., 1892, 590). —The oil resulting from the action of ethylic sodiomalonate on ethylic acetylenedicarboxylate yields aconitic acid when decomposed by baryta water, indicating that the oil has the formula

$$COOEt\cdot CH\colon C(COOEt)\cdot CH(COOEt)_2.$$

The action of ethylic acetylenedicarboxylate on ethylic sodethenyltricarboxylate yields a viscid oil,

$$COOEt\cdot CH\colon C(COOEt)\cdot CH(COOEt)\cdot CH_2\cdot COOEt.$$

Ethylic phenylpropiolate and ethylic sodiomalonate yield a pale yellow oil, $COOEt\cdot CH\colon CPh\cdot CH(COOEt)_2$, from which a phenylglutaconic acid, $COOH\cdot CH_2\cdot CPh\colon CH\cdot COOH$, crystallising in prismatic plates, and melting at 154—155°, can be obtained by treatment with baryta water.

Benzalacetone and ethylic sodiomalonate yield the ethylic salt $CH_2Ac\cdot CHPh\cdot CHAc\cdot COOEt$, which crystallises in white needles or prisms, melts with decomposition at 155—157°, and dissolves in organic solvents; when decomposed by potash solution, it yields a colourless oil, $C_{13}H_{14}O$, which boils at 197—198·5°.

The author concludes with the following generalisation. Unsaturated compounds of the constitution $R\cdot \overset{.}{C}H\cdot \overset{.}{C}H\cdot X$, or $R\cdot \overset{.}{C}\cdot \overset{.}{C}\cdot X$ [ethylene and acetylene unions being indicated in this way throughout the paper], wherein R is a positive or negative organic radical, and X a strongly negative radical, such as CN, CHO, COOEt, &c., act on ethylic sodiomalonate and sodacetoacetate and their derivatives in

such a manner that the sodium, in accordance with the positive-negative rule, attaches itself to the unsaturated negative carbon, and the remainder of the compound attaches itself to the relatively positive unsaturated carbon atom. A. G. B.

Allofurfuracrylic Acid and the Formation of Allo-Acids. By C. LIEBERMANN (*Ber.*, **27**, 283—289; compare Abstr., 1893, i, 513).—Allocinnamic acid, which is formed to the extent of about 5 per cent. when benzalmalonic acid is melted, is not formed at all, or only in traces, when the acid is decomposed at lower temperatures by heating with aniline or quinoline. When benzalmalonic acid is boiled with acetic anhydride, carbonic anhydride is eliminated, and the product contains about 5 per cent. of the allo-acid. The application of this treatment with acetic anhydride to furfuralmalonic acid, on the other hand, resulted in the production of about equal weights of furfuracrylic acid and of its allo-modification. Furfuralmalonic acid, originally prepared by Marckwald (Abstr., 1888, 678), is best obtained by heating furfuraldehyde with malonic acid and glacial acetic acid. It melts at about 205° with decomposition, and not at 187°, as stated by Marckwald. *Furfuracrylic acid* is readily soluble in hot benzene, but dissolves in 77 parts of benzene at 19°. When slowly distilled, it decomposes, with formation of *furfurethylene*, $C_4OH_3 \cdot CH \colon CH_2$, which alone passes over into the receiver. This substance is a mobile, colourless liquid, which has an odour resembling that of cinnamene, and boils at 99°. It is insoluble in water, and readily combines with bromine.

Allofurfuracrylic acid is formed, together with the acid just described, when furfuralmalonic acid is heated with acetic anhydride. Like allo-cinnamic acid, it is much more readily soluble than the ordinary form, from which it can therefore be easily separated. It crystallises from light petroleum in needles, and melts indefinitely at 83—87°. The *silver salt* is a white, crystalline precipitate, which is not quite insoluble in water.

The acid readily combines with bromine, and gives a yellowish-red coloration with ferric chloride. Concentrated hydrochloric or sulphuric acid converts it into a resin. When slowly distilled, it yields furfurethylene, but when rapidly heated the distillate contains about 2 parts of furfuracrylic acid to 1 part of the allo-acid. This change proceeds more readily in benzene solution at 170°.

The allo-form of cinnamylacrylic acid will form the subject of a further communication. A. H.

Formation of Closed Chain Compounds from Open Carbon Chains. By W. DIECKMANN (*Ber.*, **27**, 102—103).—By the action of sodium on ethylic adipate in molecular proportion at 120°, *ethyl β-ketopentamethylenecarboxylate*, $CH_2{<}^{CH_2 \cdot CO}_{CH_2 \cdot CH \cdot COOEt}$, is formed, it yields a green *copper salt*, and produces, in alcoholic solution, a deep blue coloration with ferric chloride. On hydrolysis with dilute sulphuric acid, ketopentamethylene is obtained, and was identified both by its own properties and by those of its oxime. Ethylic

pimelate yields, in a similar manner, *ethylic β-ketohexamethylenecarb-oxylate*, $CH_2 \big\langle {}^{CH_2 \cdot CO-}_{CH_2 \cdot CH_2} \big\rangle CH \cdot COOEt$, which may be readily converted into ketohexamethylene. These results are in complete harmony with v. Baeyer's theory of the formation of closed carbon chains.   J. B. T.

Constitution of Benzene. By A. CLAUS (*J. pr. Chem.*, [2], **48**, 576—595).—A dissertation on the appropriateness of the author's diagonal formula, with special reference to the work of Marckwald (Abstr., 1893, i, 603).   A. G. B.

Reduction by means of Sodium and Alcohol. By A. LADENBURG (*Ber.*, **27**, 78).—Whilst not the originator of this method, the author claims to have been the first to systematically determine the conditions necessary for its advantageous employment, he considers, therefore, that it should bear his name (comp. Einhorn and Willstätter, this vol., i, 87).   J. B. T.

Reduction Products of Benzene. By A. v. BAEYER (*Annalen*, **278**, 88—116).—Berthelot (*Bull. Soc. Chim.*, 1867—68) obtained hexane (b. p. 69°) by heating benzene in a sealed tube at 280° with an excess of fuming hydriodic acid. Baeyer (*Annalen*, **155**, 266) and Wreden (*Annalen*, **187**, 153) confirmed this observation, and found that benzene cannot be reduced by phosphonium iodide at 350°. Kijner (Abstr., 1893, i, 150, 460) observed that the oil obtained by Berthelot's method is a mixture of hexane and hexahydrobenzene, and that when benzene (1 c.c.) is heated with fuming hydriodic acid (25 c.c.) at 260—270°, the product consists entirely of hexahydrobenzene. Independently of the fact that the reduction of benzene appears to give hexane as well as hexahydrobenzene, the process is complicated and costly. For these reasons, the author has employed diketohexamethylene as the starting point for the preparation of the hydrogenised derivatives of benzene. His experiments have been already published to some extent (see Abstr., 1892, 833, 1074; 1893, i, 254).

Diketohexamethylene is reduced to quinitol (Abstr., 1892, 833) by sodium amalgam. The product is acetylated and distilled under diminished pressure; the solid *trans-diacetylquinitol* is separated from the *cis*-modification by filtration. The former melts at 102—103°, and the latter at 34—36°. When these acetyl derivatives are boiled with barium hydroxide, *trans-quinitol*, melting at 139°, and *cis-quinitol*, melting at 100—102°, are respectively obtained. They are both colourless crystalline compounds, having a sweet taste at first, which is followed by a bitter one. Their other properties agree with that of the mixture already described (*loc. cit.*). When heated in a sealed tube with fuming hydrobromic acid, the two stereoisomerides yield two *paradibromhexamethylenes*, $C_6H_{10}Br_2$; the *trans*-modification melts at 113°, whilst the *cis*-modification is liquid.

Dihydrobenzene (Abstr., 1892, 1074), when pure, boils at 84—86° (corr.), under a pressure of 718 mm.; the spectroscopic examination of the characteristic blue coloration which it gives with alcoholic

sulphuric acid is described. *Dihydrobenzene tetrabromide* melts at 184—185°.

When quinitol is heated with fuming hydriodic acid in a sealed tube at 100°, *trans-paradiiodohexamethylene*, melting at 144—145°, is obtained, together with the liquid *cis*-modification. *Quinitol iodohydrin* is formed, together with the last-mentioned diiodide, by evaporating a solution of quinitol with dilute hydriodic acid ; the crude product, if distilled with quinoline (5 parts), is converted into a mixture of dihydrobenzene and tetrahydrophenol ; the latter is a mobile liquid which boils at 166° (corr.) under a pressure of 716 mm., and has the odour of caprylic alcohol, especially when it is warmed with water, which dissolves considerable quantities. It instantaneously reduces permanganate, and behaves towards Bechmann's chromic acid solution (*Annalen*, **250**, 325) in the same manner as hydroxyhexamethylene. The *phenylurethane* melts at 79°. *Hydroxyhexamethylene* is obtained when the crude mixture of iodhydrin and diiodide is reduced with glacial acetic acid and zinc dust in the cold ; it melts at 16—17°, and boils at 160—161° (corr.) under a pressure of 716 mm. It has the odour of fusel oil, is stable towards cold permanganate, and when warmed with nitric acid is oxidised to adipic acid. The *acetyl* derivative is an oil having the odour of amylic acetate, which boils at 175—177° (corr.) under a pressure of 720 mm. The *phenylurethane* melts at 80—81°. When hydroxyhexamethylene is treated with Bechmann's reagent (*loc. cit.*), it yields ketohexamethylene, identical with that obtained by distilling calcium pimelate (Mager, Abstr., 1893, 558), and with that prepared by Drechsel, by electrolysing phenol with alternating currents (Abstr., 1888, 1277). It boils at 155—156° (corr.) under a pressure of 716 mm., has the odour of peppermint, and its sp. gr. at about 21° is 0·952 ; the pure compound gives no coloration with Millon's reagent. The *oxime* melts at 88°. When the ketone is heated with ammonium formate in a sealed tube at 190—200°, or when the oxime is reduced with sodium and alcohol, *hexamethylenamine* is obtained. It is a colourless liquid, having an odour resembling that of coniine ; the *hydrochloride* melts at 204° ; the *aurochloride* at 190—191°. The *acetyl* derivative melts at 104°, the *benzoyl* derivative at 147°, the *phenylureïde* at 180°, and the *phenylthiureïde* at 147—148°.

Ketohexamethylene forms a phenylhydrazone melting at 74—77° with decomposition, which, when warmed with mineral acids, yields Graebe and Glaser's hydrocarbazole ; it melts at 114° (not 120°). Hydroxyhexamethylene is obtained when ketohexamethylene is reduced with sodium and moist ether. If the hydroxy-compound is heated with fuming hydrobromic or hydriodic acid, *bromhexamethylene*, boiling at 165—166° (corr.) under a pressure of 714 mm., and *iodhexamethylene*, boiling at 180°, are respectively produced.

When bromhexamethylene is warmed with quinoline (5 parts), *tetrahydrobenzene*, boiling at 82—84° under a pressure of 715 mm. (see also Abstr., 1893, i, 255), is obtained. The *dibromide* boils at 215—220°, with slight decomposition ; the nitrosate, $NO \cdot C_6H_{10} \cdot ONO_2$, forms white needles and melts at 150° with decomposition, and the *nitrosite*, $NO \cdot C_6H_{10} \cdot ONO$, also melts at about 150° with decomposition.

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Hexamethylene (*hexahydrobenzene*) is obtained by reducing iodhexamethylene with zinc dust and acetic acid in the cold. The crude product is freed from unsaturated compounds by shaking it with cold, aqueous, 3 per cent. permanganate; it has a petroleum-like odour, and boils at 79—79·5° (corr.) under a pressure of 718 mm.

The paper concludes with a general discussion of the results obtained up to the present. So far as our present knowledge extends, the derivatives mentioned in the first column of the following table may be regarded as the parent compounds of those in the second.

Dihydrobenzene,	Terpene,
Tetrahydrobenzene,	Menthene,
Hexahydrobenzene,	Hexahydrocymene,
Quinitol,	Terpinol,
Tetrahydrophenol,	Terpineol,
Hexahydrophenol,	Menthol,
Ketohexamethylene.	Menthone.

The values given in the following table are approximate.

	Increase in heat of combustion.	Increase or decrease in boiling point.
Benzene to dihydrobenzene......	68·2 cal.	+5·0°
Dihydro- to tetrahydro-benzene..	44·0 ,,	—2·5
Tetrahydro- to hexahydro-benzene	41·2 ,,	—3·5
Hexahydrobenzene to hexane	58·0 ,,	—10·0

A. R. L.

Action of Water on Tribromotrinitrobenzene and on Tribromodinitrobenzene. By C. L. JACKSON and W. H. WARREN (*Amer. Chem. J.*, **16**, 28—35; compare Abstr., 1892, 1182).—Symmetrical tribromotrinitrobenzene (m. p. 285°) is converted on boiling with sodium carbonate and water into a mixture of the sodium salts of trinitrophloroglucinol and a new *tribromodinitrophenol*,

$$C_6Br_3(NO_2)_2 \cdot OH.$$

The latter crystallises from dilute alcohol in pale, yellow, square-ended needles, is readily dissolved by most of the ordinary solvents, forms a characteristic barium salt, and melts at 194°. Tribromodinitrobenzene (m. p. 192°) prepared from symmetrical tribromobenzene gives, under the same conditions, a dibromodinitrophenol, which melts at 147—148°, a temperature almost identical with that (146—146·5°) of the only other known dibromodinitrophenol, which has been recently described by Garzino (*Atti. R. Accad. Sci. Torino*, **25**, 263), and is obtained by the action of nitric acid on the propionic derivative of metabromophenol. The identity, however, is only apparent, as Garzino's compound gives barium and potassium salts differing markedly from the salts of the new compound. Mixed with the dibromodinitrophenol above described is an oily phenol, which was not obtained in a pure state.

Tribromotrinitrobenzene and tribromodinitrobenzene are, therefore, decomposed by water and sodium carbonate in the same general

manner as with sodium ethoxide, the trinitro-compound in both cases showing two parallel reactions, in one of which nitro-groups, in the other bromine atoms, are removed, whilst the dinitro-compound in both cases loses part of its bromine. It is to be noted, however, that whilst the ethoxide removes two nitro-groups from the trinitro-, and two bromine atoms from the dinitro-compound, water in each of these cases removes only one, although, like the ethoxide, it removes all three of the bromine atoms from the tribromotrinitrobenzene.

The constitution of the new tribromodinitrophenol can be only $Br_3 : (NO_2)_2 = 2 : 4 : 6 : 3 : 5$, as the substance from which it is derived is symmetrical. The dibromodinitrophenol, on the other hand, can be either $OH : Br_2 : (NO_2)_2 = 1 : 3 : 5 : 2 : 4$, or $= 1 : 3 : 5 : 2 : 6$, but which it is has not yet been determined. G. T. M.

New Class of Compounds resulting from the Action of Iodine in Presence of Alkali on Phenols. By T. R. CARSWELL (*Chem. News*, **68**, 87—89, 99—101, 131—132, 153—155, 166—167, 181—183, 195—196, 203, 214—216, 227—228).—The author refers to the researches of Messinger (Abstr., 1887, 1150, *et seq.*). He states that he has obtained several new derivatives by the action of iodine in presence of alkali on various phenolic compounds, and gives analytical data. A. R. L.

Dihydroresorcinol. By G. MERLING (*Annalen*, **278**, 20—57).—*Dihydroresorcinol*, $C_6H_8O_2$, is obtained when 2 per cent. sodium amalgam (5 kilos.) is gradually added to a solution of resorcinol (100 grams) in water (1 litre) at 90°, a current of carbonic anhydride being passed through the solution meanwhile; the alkaline liquid is acidified with dilute sulphuric acid, filtered, and the filtrate extracted with ether. After distilling off the ether, the compound remains as a syrup which, on being cooled, solidifies; the crystals are washed with anhydrous ether. It crystallises from benzene in colourless, lustrous prisms, and melts at 104—106° with loss of water and formation of the *compound*, $C_{12}H_{14}O_3$; the aqueous solution has an acid reaction, decolorises permanganate, gives an intense violet-red coloration with ferric chloride, and reduces ammoniacal silver solution, but not Fehling's solution. The *sodium*, *barium*, and *calcium* salts were prepared; the *silver salt*, $C_6H_7O_2Ag$, crystallises from hot water in grey, lustrous needles. Dihydroresorcinol forms condensation compounds with aldehydes; that obtained from formaldehyde has the formula $CH_2(C_6H_7O_2)_2$, and melts at 132—133°.

Glutaric and succinic acids are formed when dihydroresorcinol is oxidised with alkaline permanganate. The production of glutaric acid explains the structure of dihydroresorcinol, whilst a consideration of the facts described below indicates that it is a tautomeric compound

thus, $CH_2 {<}^{CH_2----CO}_{CH_2 \cdot C(OH)} {>} CH$ or $CH_2 {<}^{CH_2 \cdot CO}_{CH_2 \cdot CO} {>} CH_2$.

The *dioxime*, $C_6H_8(NOH)_2 + 2H_2O$, is rendered anhydrous when kept over concentrated sulphuric acid, and then melts at 154—157°, decomposing at about 200°; it reduces Fehling's solution when boiled with it. *Metadiamidohexamethylene*, $C_6H_{10}(NH_2)_2$, is obtained by re-

ducing the dioxime with sodium and boiling alcohol; it is a colourless oil which fumes slightly in the air, mixes in all proportions with water, is soluble in anhydrous, but not in moist ether, boils at 193° (752 mm.), and its sp. gr. at 15° is 0·956. The *platinochloride* melts with decomposition at 255°, and the *diacetyl* derivative forms colourless needles, and melts at 256°.

Dihydroresorcinol phenylhydrazone, $C_6H_8O:N\cdot NHPh$, is precipitated on adding aqueous phenylhydrazine to a solution of dihydroresorcinol; it crystallises in colourless needles, melts at 176—177°, and reduces Fehling's solution when boiled with it. If a solution of dihydroresorcinol is gently heated with an excess of phenylhydrazine, the *azo*-compound, $NHPh\cdot N:C_6H_7\cdot N:NPh$, is obtained; it crystallises from alcohol in garnet-red prisms.

Chlorotetrahydroresorcinol, $CH_2 <^{CH_2---CO}_{CH_2\cdot CH(OH)}> CHCl$, separates as a colourless, crystalline powder when hydrogen chloride is passed into a solution of dihydroresorcinol in chloroform; it is stable towards air, readily dissolves in water, forming dihydroresorcinol, but is almost insoluble in ether, chloroform, and benzene. If a solution of dihydroresorcinol in chloroform is treated with bromine in the cold, *dibromotetrahydroresorcinol* is obtained. It is a highly unstable compound, readily losing hydrogen bromide when boiled with water, *bromodihydroresorcinol*, $CH_2 <^{CH_2---CO}_{CH_2\cdot C(OH)}> CBr$, separating from the aqueous solution on cooling; this melts at 166° with evolution of hydrogen bromide, decomposes solutions of alkali carbonates, reacts with phenylhydrazine in the same manner as dihydroresorcinol, but appears not to form an oxime. It does not unite with bromine, but, when treated with the latter, *bromoresorcinol*, $C_6H_3Br(OH)_2$, is formed; when heated with phthalic anhydride (5 parts) fluoresceïn is obtained.

When the silver salt of dihydroresorcinol is treated with alkylic iodides or bromides, alkyl derivatives, $CH_2 <^{CH_2---CO}_{CH_2\cdot C(OR')}> CH$, are produced; they are colourless oils, devoid of odour, the *methyl* derivative being soluble in water, whilst the *ethyl* and *allyl* derivatives are insoluble in water. They are all decomposed by water into the alcohol and dihydroresorcinol, the more readily in presence of hydroxylamine; hence attempts to prepare oximes were unsuccessful. Monacetyl and monobenzoyl derivatives (not di-derivatives) can be prepared, but they are even more unstable towards water than the last-mentioned alkyl derivatives. Dihydroresorcinol dissolves in acetic chloride, forming chlorotetrahydroresorcinol (see above).

Dihydroresorcinol dicyanhydrin, $CH_2 <^{CH_2\cdot C(OH)(CN)}_{CH_2\cdot C(OH)(CN)}> CH_2$, is obtained by adding hydrochloric acid to an intimate mixture of dihydroresorcinol and potassium cyanide cooled by ice, dissolving the product in a small quantity of water, and extracting with ether. It dissociates in 2 per cent. aqueous solution into dihydroresorcinol and hydrogen cyanide, and when the latter is removed by a continuous current of air, the dissociation is practically complete after some

hours. The compound dissolves in hydrochloric acid of sp. gr. 1·19, but the temperature soon rises; if care is taken not to allow it to exceed 45°, a magma is obtained consisting of ammonium chloride and *dihydroxyhexahydroisophthalimide*, $CH_2{<}{CH_2 \cdot C(OH) \over CH_2 \cdot C(OH)}{>}{CH_2 \cdot CO \over CH_2 \cdot CO}{>}NH$; the latter crystallises from boiling water in lustrous prisms, melts at 272—273° with evolution of gas, and is readily soluble in alkalis. *Dihydroxyhexahydroisophthalic acid*, $CH_2{<}{CH_2 \cdot C(OH)(COOH) \over CH_2 \cdot C(OH)(COOH)}{>}CH_2$, is formed when the last compound is boiled for a short time with hydrochloric acid; it crystallises in delicate needles or lustrous prisms, melts at 217—218° with evolution of gas, is sparingly soluble in cold water, and as good as insoluble in alcohol and ether. The *barium* salt crystallises with $4H_2O$; if it is boiled with dilute sulphuric acid and the filtrate evaporated, *dihydroxyhexahydroisophthalic anhydride* is obtained; this crystallises from glacial acetic acid in lustrous prisms, melts at 174—176°, and is readily soluble in water. When dihydroxyhexahydroisophthalimide is heated with zinc dust, pyrroline, ammonia and indifferent compounds are formed, whilst if it is boiled with sodium and amylic alcohol, an oily base, not miscible with water, is obtained, together with piperidine.

A. R. L.

Oxidation of Amido-Bases by Sodium Peroxide. By O. FISCHER and J. TROST (*Ber.*, **26**, 3083—3085).

—The oxidation of amido-bases with sodium peroxide proceeds in a different manner in acid and in alkaline solution; in the former case, the products are usually of a complicated nature, whilst in alkaline solution the amido-group is converted into the nitro-group. Thus, aniline in this manner yields nitrobenzene, and the phenylenediamines are all converted into the corresponding nitranilines. Orthoparatoluylenediamine differs from these, inasmuch as, by the action of an excess of sodium peroxide, both amido-groups may be converted into nitrogroups.

H. G. C.

Diacetyl-derivatives of certain Aromatic Amines. By F. ULFFERS and A. v. JANSON (*Ber.*, **27**, 93—101).

—The following compounds have been prepared in order to ascertain the relative facility with which the acetyl derivatives of certain amines are formed, and also the influence of substituting groups on the reaction. *Diacetylbromaniline*, $C_6H_4Br \cdot NAc_2$ [1 : 4], is prepared by heating acetylparabromaniline with acetic anhydride for eight hours at 205—210°, and crystallises from light petroleum in aggregates of needles or prisms, melting at 74—74·5°. *Diacetylbromotoluidine*,

$$C_6H_3MeBr \cdot NAc_2 \ [N : Br : Me = 1 : 2 : 4],$$
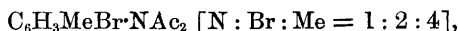
is prepared from the acetyl derivative at 150—160°, and crystallises in large, flat prisms, which melt at 75—75·5°. *Diacetyldibromaniline*, $C_6H_3Br_2 \cdot NAc_2$ [N : Br : Br = 1 : 2 : 4], is formed from the acetyl com-

pound by heating for 6 hours at 200°; it crystallises in hard plates and melts at 54—55°. *Acetyldibromotoluidine*, $C_6H_2Br_2Me\cdot NHAc$ [N : Br : Br : Me = 1 : 2 : 6 : 4], is formed at 100° and crystallises in large flat prisms, melting at 199—200°. The *diacetyl derivative* is deposited in thick plates or prisms melting at 101—101·5°. *Diacetyltribromaniline*, $C_6H_2Br_3\cdot NAc_2$ [N : Br : Br : Br = 1 : 2 : 4 : 6], melts at 127—128° instead of 123° as stated by Remmers. *Diacetylnitrobromotoluidine*, $NO_2\cdot C_6H_2MeBr\cdot NAc_2$ [N : Br : Me : NO_2 = 1:2:4:6], crystallises in large, pale, greenish-yellow prisms, melting at 79°.

The following compounds were all prepared by heating the amine (1 mol.) with acetic anhydride (6—7 mol.) for 10 hours at 200°, in order to ascertain the relative quantities formed. The yields are given in per cent. of the theoretical. *Diacetylnitraniline*, [$NAc_2 : NO_2$ = 1 : 4], crystallises in large, flat, pale-yellow plates, and melts at 128·5—129°. The yield is 15—20 per cent. *Diacetylnitrotoluidine*, [N : NO_2 : Me = 1 : 2 : 4] forms lemon-yellow prisms, melting at 78°. The yield is 30—35 per cent. *Diacetyldinitraniline*, [$NAc_2 : (NO_2)_2$ = 1 : 2 : 4], is deposited in pale-yellow crystals and melts at 112—113°. The yield is about 20 per cent. *Diacetyldinitrotoluidine*, [$NAc : (NO_2)_2$: Me =1 : 2 : 6 : 4] crystallises in thick, lemon-yellow plates, and melts at 129·5°. The yield is 70—80 per cent. The above results show that the monacetyl derivatives are first formed and are then converted into the diacetyl compounds, but the reaction is influenced by the nature, number, and position of the substituting groups. The brominated amines react much more readily than the corresponding nitroamines; an increase in the number of bromine-atoms or nitrogroups retards the entrance of the acetyl-groups. Diacetyl derivatives are formed with greater difficulty than monacetyl compounds; the presence of negative groups generally hinders the reaction, especially in the para-position, but in the ortho-position relative to the amidogroup, they facilitate the formation of acetyl derivatives.

<div align="right">J. B. T.</div>

Trianilidodinitrobenzene and Related Compounds. By C. L. JACKSON and H. N. HERMAN (*Amer. Chem. J.*, 16, 35—43; compare Abstr., 1890, 497; 1892, 1217). —Numerous attempts to prepare a second modification of trianilidotrinitrobenzene, or of ethylic anilidotrinitrophenylmalonate have, without exception, led to negative results, as no change of the full yellow colour or the crystalline form of either of these substances could be observed. This result is remarkable in view of the occurrence of two modifications of trianilidodinitrobenzene and of ethylic anilidotrinitrophenyltartronate.

When trianilidodinitrobenzene is crystallised from a mixture of benzene and alcohol, it appears in two forms; one, the nearly square prisms of an orange colour, like that of potassium dichromate, already described (*loc. cit.*); the other, yellow, like potassium chromate, in bladed crystals, or plates looking like flattened monoclinic prisms, terminated by two planes, or, less commonly, with square ends, which, when the cooling takes place rapidly, appear in circular groups of little needles. These two varieties, differing so widely in physical form and colour, melt at the same temperature, 179°, the yellow

modification previously becoming orange-coloured at 140°. The yellow variety is obtained by crystallisation of the substance from a solvent containing a relatively large proportion of benzene; it cannot. however, be completely freed from admixture with the orange-red crystals, which are the sole product of recrystallisation from a solvent containing very little benzene. That the two varieties are not polymeric is shown by their producing the same depression in the freezing point of a benzene solution. The numbers obtained in both cases agree closely with that required for a molecular weight corresponding with the formula $C_6H(NHPh)_3(NO_2)_2$. In all probability the two modifications are physical isomerides, or perhaps the substance is dimorphous.

Trianilidodinitrobenzene forms a remarkable additive product with chloroform, $C_6H(NHPh)_3(NO_2)_2,CHCl_3$, which is readily obtained on allowing a solution of the nitro-compound in chloroform and alcohol to evaporate at temperatures between 50° and 70°. It crystallises in well-characterised prisms, of a dark brownish-red colour, not unlike that of potassium ferricyanide, and loses part of its chloroform at ordinary temperatures, but is not completely freed from it until heated to 100°.

Triparatoluidodinitrobenzene, $C_6H(NH·C_7H_7)_3(NO_2)_2$, melts at 197°, and forms an additive product with chloroform very similar to that above described. It crystallises in brownish-red plates and in yellow, thread-like, felted crystals, the latter becoming red at 180°, and also melting at 197°.

Triorthotoluidodinitrobenzene crystallises in red, stout-pointed needles, melts at 243°, and does not appear to exist in two modifications.
G. T. M.

Bromine Derivatives of Metaphenylenediamine. By C. L. JACKSON and S. CALVERT (*Ber.*, **27**, 20).—The authors have obtained the tribromophenylenediamine, melting at 157°, which has been described by Vaubel (Abstr., 1893, i, 560), by the action of the calculated amount of bromine on a solution of the hydrochloride of metaphenylenediamine, or a mixture of the free base and water. *Diacetyltribromophenylenediamine*, $C_6HBr_3(NHAc)_2$, melts above 330°. Metaphenylenediacetamide when treated with bromine only, takes up two atoms of bromine, forming *diacetyldibromometaphenylenediamine*, which melts at 260°. The corresponding *diamine* melts at 136°.
A. H.

Diacetanilide. By A. BISTRZYCKI and F. ULFFERS (*Ber.*, **27**, 91—93).—Diacetanilide is prepared by heating acetanilide (1 mol.) with acetic anhydride (2 mol.) in a sealed tube for 8—10 hours at 200—205°. The yield is 90 per cent. of the theoretical. The properties of the compound agree with the description given by Kay (this vol., i, 76). The physiological properties of diacetanilide are in every way identical with those of acetanilide.
J. B. T.

Tartaric and Citric Derivatives of Benzylamine. By E. GIUSTINIANI (*L'Orosi*, **16**, 253—258; compare Abstr., 1893, i, 264).—*Benzyltartarimide*, $CH_2Ph·N{<}^{CO·CH·OH}_{CO·CH·OH}$, is extracted by boiling

water from the product obtained on heating tartaric acid with benzyl-amine at 165°; it forms white, crystalline laminæ melting at 196°, is very soluble in alcohol or acetic acid, and gives an oily *nitro*-deriva-tive when treated with fuming nitric acid. On dissolving the imide in concentrated potash and acidifying, *benzyltartramic acid*,

$$CH_2Ph \cdot NH \cdot CO \cdot CH(OH) \cdot CH(OH) \cdot COOH,$$
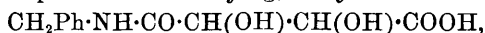
separates; it crystallises in thin, white needles melting at 166°, and is readily reconverted into the imide by hot, dilute hydrochloric acid. The *barium* salt forms lustrous, white crystals containing $1H_2O$, which is given off in a vacuum or at 100°. Both the acid and the imide yield acetyl and benzoyl derivatives.

Benzylamine citrate crystallises in long needles which contain water, melts at 110°, and on heating at 155°, yields *monobenzylcitrimide*, $C_4H_6O_3 {<}{}^{CO}_{CO}{>} N \cdot CH_2Ph$; this is very soluble in alcohol, and crystal-lises in yellowish laminæ, which soften at 189°, and melt at 197°; it gives off benzylamine on heating with caustic alkali, and also yields an *acetyl* derivative. On gently warming the imide with aqueous ammonia, and decomposing the cooled solution with acetic acid, *monobenzylcitramic acid*, $CH_2Ph \cdot NH \cdot CO \cdot C_4H_6O_3 \cdot COOH$, is de-posited; it is best prepared by dissolving the imide in baryta solu-tion, and precipitating with the exact quantity of sulphuric acid. It forms colourless leaflets melting at 165° with decomposition, and is soluble in water, alcohol, or ether. The *barium* salt forms small, lamellar crystals containing $2H_2O$, which is lost at 100°.

Monobenzylaconitimide (?) sublimes in yellowish needles on heating benzylcitrimide at 230° in a current of carbonic anhydride; it com-bines with bromine to give an oily *compound*, which easily loses hydrogen bromide, yielding *monobrombenzylcitraconimide* (?),

$$C_{13}H_{10}BrNO_4. \qquad W. J. P.$$

Isobutenylphenylamidine. By O. HINSBERG and F. FUNCKE (*Ber.*, **26**, 3092—3094).—From the result of his investigations, Hins-berg concluded many years ago that the orthodiamines and aldehydes always interact with formation of anhydro-bases, and, with one exception, subsequent investigation has confirmed the rule. Lassar-Cohn, however (Abstr., 1890, 138), by the action of isobutyr-aldehyde on orthodiamidobenzene, obtained a substance to which he ascribed the formula $C_{10}H_{14}N_2$, and containing, therefore, 2 atoms of hydrogen more than the anhydro-base, isobutenylphenylamidine, $C_6H_4 {<}{}^{-\ N}_{NH}{>} CPr^\beta$. The authors have, therefore, reinvestigated this reaction, and find that the anhydro-base is in reality formed, and that Lassar-Cohn's statement is incorrect.

The compound described by Griess as gluco-orthodiamidobenzene (Abstr., 1887, 475, 930) is, according to the authors, in all prob-ability also an anhydro-base. H. G. C.

Action of Diazobenzene on Acetaldehyde, Pyruvic acid, and the Hydrazone of the latter. By E. BAMBERGER and J. MÜLLER

(*Ber.*, **27**, 147—155).—In alkaline solution, diazobenzene reacts with acetaldehyde, forming phenylazoformazyl, $C(N_2Ph)_2:N_2HPh$, together with formic acid and water; phenylazoformazyl is best prepared in this way. It yields explosive metallic derivatives, and a yellow *acetyl derivative* melting at about 190°.

With pyruvic acid, *formazylglyoxalic acid*,

$$N_2HPh:C(N_2Ph)\cdot CO\cdot COOH,$$
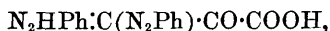
is the chief product, but some phenylazoformazyl and oxalic acid are also formed; these can be shown to be produced by the action of diazobenzene on formazylglyoxylic acid. This acid forms red needles melting at 166°; it yields explosive, metallic derivatives, also a *methylic salt* in red needles melting at 124—125°, and an *ethylic salt* as red plates or cubes melting at 105—106°. With acetic anhydride and zinc chloride, it does not yield an acetyl derivative, but is transformed into an isomeric substance, which crystallises in yellow needles, and melts at 158—163°. Its *phenylhydrazone* is a dark brown powder, and, when heated in acetic acid solution, it yields a mixture of *phenylazophenylketopyrazolonephenylhydrazone*,

$$NPh{<}^{N\!=\!C\cdot N_2Ph}_{\ CO\cdot C:N_2HPh},$$

which forms red needles melting at 216—217°,

and *phenylazophenylosotriazolecarboxylicacid*, $NPh{<}^{N:C\cdot N_2Ph}_{N:C\cdot COOH}$, which

crystallises in orange-yellow plates melting at 195—196°, and yields metallic salts, often explosive. Formazylglyoxalic acid is, finally, converted by boiling hydrochloric acid into phenazine,

$$C_6H_4{<}^{N}_{N}{>}C_6H_4.$$
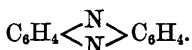
With pyruvic acid hydrazone, diazobenzene, in alkaline solution, yields *methylformazyl*, $N_2Ph\cdot CMe:N_2HPh$, a substance which forms long, orange needles melting at 120—121°, and, unlike hydrogen formazyl, is easily oxidisable. It appears also to be formed when alkaline diazobenzene reacts with methylacetoacetic acid.   C. F. B.

Action of Diazobenzene on Nitromethane. By E. BAMBERGER (*Ber.*, **27**, 155—160).—The product of the reaction, when the latter is carried out in alkaline solution, is not "azonitromethylphenyl," as Friese thought (Abstr., 1876, i, 85), but *nitroformazyl*,

$$N_2Ph\cdot C(NO_2):N_2HPh.$$

It exhibits all the properties of formazyl compounds, and has in addition strong acid properties. Further, when heated with alkaline diazobenzene, it yields phenylformazyl, $N_2Ph\cdot CPh:N_2HPh$.

The compound that Friese was looking for, and which is probably not an azo-compound, but a hydrazone—nitroformaldehydehydrazone, $NO_2\cdot CH:N_2HPh$, can be obtained, together with some nitroformazyl, by allowing diazobenzene to react with potassio-nitromethane in a slightly acid solution. It crystallises in yellow needles melting at 84—85°, and yields a silver derivative.   C. F. B.

Action of Diazobenzene on Acetonecarboxylic acid. By H. v. PECHMANN and L. VANINO (*Ber.*, **27**, 219—224).—Since it has been shown that diazobenzene yields, with certain fatty derivatives, not azo-, but hydrazo-compounds, a different constitution must be assigned to the substances described in Abstr., 1892, 161. The "disbenzeneazoacetone," there described as obtained by the action of diazobenzene on acetonecarboxylic acid, is really *propanon-diphenylhydrazone*, $CO(CH:N_2HPh)_2$, as it is shown by the fact that its diacetyl derivative yields acetanilide when treated with alkalis, from which it follows that the acetyl group must be attached to the nitrogen atom, and, consequently, that the original compound is a hydrazone, and not an azo-compound. This *diacetyl derivative*, $CO(CH:N_2AcPh)_2$, forms lemon-yellow needles melting, with decomposition, at 167—168°. *Propanon-diparatolylhydrazone*,
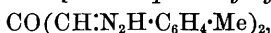
$$CO(CH:N_2H\cdot C_6H_4\cdot Me)_2,$$

is obtained from acetonedicarboxylic acid and paradiazotoluene, and forms red needles melting, with decomposition, at 192—193°. *Propanon-diparachlorophenylhydrazone*, $CO(CH:N_2H\cdot C_6H_4Cl)_2$, from the same acid with parachlorodiazobenzene, forms red needles shot with violet, and melts at 191°.

Propanetriphenylhydrazone, $N_2HPh:C(CH:N_2HPh)$, is the correct name of the substance obtained by the action of phenylhydrazine on disbenzeneazoacetone, and previously described as the hydrazone of the latter. *Propane-1 : 2-diphenyl-3-methylphenylhydrazone*,

$$N_2MePh:C(CH:N_2HPh)_2,$$

is obtained by the action of methylphenylhydrazone; it forms lemon-yellow needles melting at 192—193°.

The substance formed when propanetriphenylhydrazone is boiled with acetic anhydride is now shown to be, not $C_{23}N_{20}N_6$, but 1-*phenyl-4-benzeneazopyrazole*, $N_2Ph\cdot C {\overset{\textstyle CH:N}{\underset{\textstyle CH\cdot NPh}{<}}}$. The diphenylmethylphenyl-hydrazone forms no such compound, but the diparachlorophenylhydrazone, when heated with phenylhydrazine and glacial acetic acid, yields 1-*parachlorophenyl-4-benzeneazopyrazole*,

$$N_2Ph\cdot C {\overset{\textstyle CH:N}{\underset{\textstyle CH\cdot N\cdot C_6H_4Cl}{<}}},$$
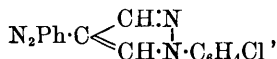
as yellow plates melting at 152.° *Acetylparachlorophenylhydrazine* is formed at the same time, and was obtained in colourless needles melting at 154°.   C. F. B.

Decomposition of Substituted Diazobenzenenimides. By P. FRIEDLÄNDER and M. ZEITLIN (*Ber.*, **27**, 192—198).—It has long been known that diazobenzenimides, when warmed with more or less dilute sulphuric acid, yield para- (or ortho-) amidophenols. The authors think that hydroxylamines are formed as an intermediate stage, for example, $C_6H_5\cdot N_3 + H_2O = N_2 + C_6H_5\cdot NH\cdot OH \rightarrow OH\cdot C_6H_4\cdot NH_2$, and they attempted to isolate these by examining diazobenzenimides in which the para-position was already occupied. They were not

successful, however, for a simple reaction does not take place, except in the case of *nitro*diazobenzenimides, which readily yield nitramidophenols, but even then no intermediate product could be isolated. In the solitary case of nitrotolyldiazimide [Me : NO_2 : N_3 = 1 : 2 : 4], a solution was obtained which contained no nitramidocresol, but yielded metatolylenediamine when reduced ; probably this solution contained nitrotolylhydroxylamine, but attempts to isolate the latter yielded only amorphous polymerisation products.

Tolyldiazimide [Me : N_3 = 3 : 4] yields amidocresol,

[OH : Me : NH_2 = 1 : 3 : 4].
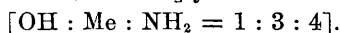
Orthonitrodiazobenzenimide [NO_2 : N_3 = 3 : 4] yields the *nitramidophenol* [NO_2 : NH_2 : OH = 3 : 4 : 5], which crystallises in small, red needles melting at 135—136°, yields a *monacetyl derivative* as yellowish-red needles, and, in alcoholic solution, is converted by nitrous acid into 3 : 5·nitrophenol. Paranitrodiazobenzenimide [NO_2 : N_3 = 1 : 4] yields the *nitramidophenol* [NO_2 : NH_2 : OH = 1 : 4 : 5] as light brown needles melting at 201—202°, convertible into 1 : 5-nitrophenol. Metanitrodiazobenzenimide [NO_2 : N_3 = 2 : 4] yields the nitramidophenol [OH : NO_2 : NH_2 = 1 : 2 : 4], which forms reddish needles melting at 126—128°, yields a *monacetyl derivative* as yellow needles melting at 157—158°, and is convertible into 1 : 2-nitrophenol.

C. F. B.

Benzenylamidoxime. By E. BAMBERGER (*Ber.*, **27**, 160—163).— An attempt was made to prepare an amidrazone, $NH_2 \cdot CPh \cdot N_2 Ph$, by the action of phenylhydrazine in acetic acid solution on benzenyl-amidoxime, $NH_2 \cdot CPh \cdot NOH$, but the product of the reaction was found to be a mixture of phenylformazyl, $N_2 Ph \cdot CPh \cdot N_2 HPh$, and benzoyl-phenylhydrazine, $CPhO \cdot N_2 H_2 Ph$.

C. F. B.

Isomerism of Derivatives of Chloroquinonemeta-oxime. By F. KEHRMANN (*Ber.*, **27**, 217—219).—Bridge (this vol., i, 25) is in error in supposing that the two benzoates and the two methylic ethers of chloroquinoneoxime are structurally isomeric. Their isomerism is geometrical only, for they are all derived from the same chloroquinone-oxime [O : Cl : NOH = 1 : 2 : 4], as is shown by the fact that both benzoates are oxidised by nitric acid to the same dinitrochlorophenol [OH : Cl : $(NO_2)_2$ = 1 : 2 : 4 : 6], and, like the two methylic ethers, are both reduced by stannous chloride to the same chloramidophenol [OH : Cl : NH_2 = 1 : 2 : 4]. It is not a case of tautomerism, nor is the isomerism of the kind existing between a " nitrogen- " and an " oxygen-ether," for both the methylic ethers are obtained by the action of methoxylamine on chloroquinone ; either of these ethers can, by heating, be partially converted into its isomeride. C. F. B.

Auramines. By A. STOCK (*J. pr. Chem.*, [2], **48**, 601).—The author has already stated (Abstr., 1893, i, 472) that the di-substituted auramines are decomposed by aqueous ammonia, partly into amines and ketones, and partly with the formation of non-substituted auramines. He now points out that the concentration of the solution has considerable influence on the change ; the greater this is, the more does the formation of an auramine become the main reaction.

A. G. B.

Action of Phosphorus Pentachloride on Urethanes. By F. LENGFELD and J. STIEGLITZ (*Amer. Chem. J.*, **16**, 70—78; compare Abstr., 1893, i, 310 and 631).—On heating phosphorus pentachloride with phenylurethane at 55°, ethylic chloride is slowly evolved, and chloroformanilide, which melts at 53—55°, and decomposes at 90—100°, is obtained (compare Hentschel, Abstr., 1885, 888). Phenylurethane first gives rise to the compound $NHPh \cdot CCl_2 \cdot OEt$, which loses ethylic chloride, giving $HNPh \cdot COCl$. This result is noteworthy, since hydrochloric acid is apparently eliminated from the chloramides more easily than alkylic chlorides from dichloroglycollic ethers.

G. T. M.

Isomerism in the Quinazoline Series. By C. PAAL and J. WEIL (*Ber.*, **27**, 34—47).—Söderbaum and Widman (Abstr., 1889, 972; 1890, 178) on the one hand, and Busch (this vol. i, 146) on the other, have described a number of derivatives of keto- and thio-tetrahydroquinazolines to which identical formulæ have been ascribed by these authors, but which differ in properties. The substance described by Paal and Bodewig (Abstr., 1891, 943) as phenylketotetrahydroquinazoline, differs from the compounds prepared by the above-named chemists and known by the same name. The authors have, therefore, re-examined the substance obtained by Paal and Bodewig, which was prepared by the reduction of orthonitrobenzyldiphenylcarbamide by tin and hydrochloric acid. The compound obtained in this manner, or by reduction of the nitro-carbamide with zinc dust and acetic acid at a low temperature, proves, however, to be *orthamidobenzyldiphenylcarbamide*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NPh \cdot CO \cdot NHPh$, and not phenylketotetrahydroquinazoline. This does not appear from the analysis of the substance, the composition of the two compounds being too nearly alike to permit of a distinction by this means, but from a determination of the molecular weight by the freezing point method and from the general behaviour of the substance. It crystallises in white needles, and, when quite pure, melts at 177°. When treated with alkaline permanganate, it is almost completely decomposed, whereas the two phenylketoquinazolines are thereby converted into the same diketo-compound. Nitrous acid converts it into a substance of acid properties, which is probably orthohydroxybenzyldiphenylcarbamide. When boiled with acetic anhydride, it is converted into orthacetamidobenzylacetanilide. When orthamidobenzyldiphenylcarbamide is heated for a short time above its melting point, it decomposes with elimination of aniline and formation of phenylketotetrahydroquinazoline, identical in every respect with the substance melting at 186—188°, described by Busch.

The *hydrochloride* of orthamidobenzyldiphenylcarbamide is a white, crystalline powder, which is moderately soluble in water and alcohol, and melts at 143—144°.

Orthanilidobenzylphenylcarbamide, $NHPh \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_2 \cdot NHPh$, is formed by the combination of phenylcarbimide with orthamidobenzylaniline in benzene solution. It crystallises in white, spherical masses or colourless needles melting at about 102°. When heated above its melting point, it decomposes into aniline and the phenylketotetrahydroquinazoline, melting at 186—188°, described by Busch.

Orthonitrobenzylparatolylphenylcarbamide,

$$NHPh \cdot CO \cdot N(C_6H_4Me)CH_2 \cdot C_6H_4NO_2,$$

is prepared by the addition of phenylcarbimide to orthonitrobenzyl-paratoluidine in benzene solution. It crystallises in light-yellow, lustrous plates melting at 119°, and is readily soluble in benzene and chloroform, less readily in alcohol. On reduction with zinc dust and acetic acid, it is converted into *orthamidobenzylparatolylphenylcarb-amide*, which is readily soluble in ether, alcohol, &c., and crystallises in druses of white needles melting at 129°. It forms crystalline salts with dilute mineral acids, and yields an acetyl compound melting at 185°.

When it is heated above its melting point, it decomposes into aniline and the paratolylketotetrahydroquinazoline of melting point 218—220°, described by Busch. A. H.

Action of Phthalic Anhydride on Paramidophenol and the corresponding Ethers. By E. CASTELLANETA (*L'Orosi*, **16**, 289—

298).—*Paramethoxyphenylphthalimide,* $C_6H_4{<}^{CO}_{CO}{>}NH \cdot C_6H_4 \cdot OMe$, is prepared by heating phthalic anhydride with paramidoanethoïl hydro-chloride at 190° or phthalic acid with paracetamidoanethoïl at 210°; it crystallises in white or yellow needles melting at 160°, and is very soluble in alcohol or acetic acid, but only sparingly in water. It yields a crystalline *nitro*-derivative which melts at 156°.

Paraethoxyphenylphthalimide is prepared by the same methods as its homologue, the corresponding phenetoïl derivatives being sub-stituted for those of anethoïl. It forms lustrous, yellow needles, melts at 204°, and is very soluble in acetic acid. Its *nitro*-derivative melts at 165°, and crystallises in yellow prisms.

On precipitating the potash solutions of the above imides with hydrochloric or sulphuric acid, the corresponding phthalamic acids are obtained; they are reconverted into the imides by heat.

Paramethoxyphenylphthalamic acid, $OMe \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_4 \cdot COOH$, forms white or yellow prisms melting at 149—150°. *Parethoxy-phenylphthalamic acid* is obtained in yellowish, acicular prisms melting at 204°. Both acids are soluble in alcohol or acetic acid, and in-soluble in water.

The author attributes the formation of both yellow and white crystals of either imide to the operation of desmotropy. W. J. P.

Nitrophenylarsen - compounds. By A. MICHAELIS and H. LOESNER (*Ber.*, **27**, 263—272).—Phenylarsinic acid, $AsPhO(OH)_2$, is not acted on by ordinary concentrated nitric acid or by the red fuming acid at 100°. It is, however, easily nitrated by the action of pure nitric acid containing 100 per cent. of HNO_3, *nitrophenylarsinic acid*, $NO_2 \cdot C_6H_4 \cdot AsO(OH)_2$, being formed. This crystallises from water in thin, rhombic plates, and decomposes when heated, water being first given off; it is readily soluble in alcohol, slightly in benzene, insoluble in ether, and is readily soluble in hot water, but only in 200 parts of water at 18°. An anhydride of the acid could not be ob-

tained, since it decomposes before the whole of the water is given off. The relative position of the nitro- and arsenic-groups has not yet been determined. When the acid is heated with bromine and water, orthonitrobromobenzene is formed.

Solutions of the acid give no precipitate with silver nitrate or mercuric chloride ; whilst lead acetate and copper sulphate produce insoluble crystalline precipitates. The alkali salts cannot be obtained in a crystalline form. The *barium salt*, $[NO_2 \cdot C_6H_4 \cdot AsO(OH) \cdot O]_2Ba$, forms crystalline crusts, whilst the *silver salt*, $C_6H_4AsNO_4Ag_2$, is a white, amorphous powder. The *calcium salt*,

$$NO_2 \cdot C_6H_4 \cdot AsO(OH) \cdot Ca \cdot OH,$$
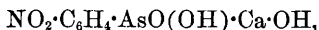
forms very slender, lustrous plates, and does not lose water when heated. The *copper salt* behaves in a similar manner, and has probably an analogous constitution.

Dinitroarsenobenzene, $NO_2 \cdot C_6H_4 \cdot As \colon As \cdot C_6H_4 \cdot NO_2$, is formed when nitrophenylarsinic acid is boiled with a solution of phosphorous acid. It is a heavy, yellow powder, which is insoluble in the usual solvents. When heated, it decomposes suddenly, and swells up, leaving a voluminous residue of carbon. Oxidising agents convert it into nitrophenylarsinic acid.

Nitrophenylchlorarsine, $NO_2 \cdot C_6H_4 \cdot AsCl_2$, is obtained by acting on dinitroarsenobenzene suspended in chloroform with chlorine, and treating the unstable *nitrophenyltetrachlorarsine*, $NO_2 \cdot C_6H_4 \cdot AsCl_4$, thus formed with a further quantity of dinitroarsenobenzene. It forms small, white crystals, melts at 46—47°, and is not altered by water. *Nitrophenylbromarsine* forms small, white crystals, readily soluble in chloroform, insoluble in light petroleum, and is not altered by water. The corresponding iodine derivative could not be obtained in the crystalline form.

Nitrophenylarsinous acid, $NO_2 \cdot C_6H_4 \cdot As(OH)_2$, is obtained by the action of alkalis on the foregoing halogen compounds. It forms a white, flocculent precipitate, which is insoluble in water, soluble in alcohol, readily soluble in alkalis, but only with difficulty in alkali carbonates. When heated, it becomes brown, and decomposes without melting.

Nitrophenylarsen disulphide, $NO_2 \cdot C_6H_4 \cdot AsS_2$, is formed when dinitroarsenobenzene is suspended in water and boiled with flowers of sulphur. It is a white power, melts at about 80°, and decomposes suddenly at a higher temperature. It is readily soluble in aqueous alkalis, slightly in alcohol, insoluble in water and ether.

Nitrophenylarsen sesquisulphide, $(NO_2 \cdot C_6H_4 \cdot As)_2S_3$, is obtained by the action of hydrogen sulphide on an aqueous solution of nitrophenylarsinic acid. It forms small, yellow crystals, melts at 119°, and decomposes suddenly at a higher temperature. It is readily soluble in alkalis, from which acids precipitate it unchanged, but is insoluble in water. Oxidising agents convert it into nitrophenylarsinic acid.

Amidophenylarsen sulphide, $NH_2 \cdot C_6H_4 \cdot AsS$, is formed when an ammoniacal solution of nitrophenylarsinic acid is treated with hydrogen sulphide. It is a white powder which softens at 182°, and melts at 188° to a yellow liquid. It is readily soluble in dilute hydrochloric

acid, but only slightly in the concentrated acid, the *hydrochloride*, $3NH_2 \cdot C_6H_4 \cdot AsS,2HCl$, being sparingly soluble in the strong acid. When boiled with hydrochloric acid, hydrogen sulphide is evolved, *amidophenylarsen chloride*, $NH_2 \cdot C_6H_4 \cdot AsCl_2$, being probably formed; this substance, however, has not been isolated. The sulphate of the amidophenylarsen sulphide, $(NH_2 \cdot C_6H_4 \cdot AsS)_3, H_2SO_4$, is a white, amorphous powder. A. H.

Betaïne and Choline of Triphenylphosphine. By A. MICHAELIS and H. v. GIMBORN (*Ber.*, **27**, 272—277).—The *chloride of the ethylic salt of triphenylphosphorbetaïne*, $PPh_3Cl \cdot CH_2 \cdot COOEt$, is obtained when ethylic chloracetate is heated with triphenylphosphine. It forms a crystalline powder, which melts at 90°, and is very readily soluble in alcohol, water, &c. The *platinochloride*,

$$(PPh_3Cl \cdot CH_2 \cdot COOEt)_2, PtCl_4,$$
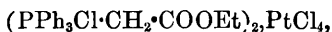
crystallises in small plates. When the ethylic salt is heated at 172°, it decomposes into its constituents. When heated at 90—100°, however, it leaves a residue of triphenylmethylphosphonium chloride. The *bromide*, $PPh_3Br \cdot CH_2 \cdot COOEt$, is obtained by mixing concentrated solutions of the chloride and potassium bromide; it melts at 147°. The corresponding *iodide* is obtained in a similar manner, and melts at 165—166°.

Triphenylphosphorbetaïne, $PPh_3 {<}^{CH_2}_{-O-}{>}CO$, cannot be prepared by the action of silver oxide or baryta water on the chloride of the ethylic salt, triphenylphosphine hydroxide, $PPh_3(OH)_2$, being thus produced. It is, however, formed when concentrated aqueous soda or sodium carbonate is used. It separates from ether in small, tabular crystals, melts at 124—126°, and is insoluble in water, readily soluble in alcohol, chloroform, and acetic acid. When heated with water, it is converted into triphenylphosphine hydroxide and acetic acid. It possesses strongly basic properties, and therefore dissolves in dilute acids. The *platinochloride*,

$$(PPh_3Cl \cdot CH_2 COOH)_2, PtCl_4,$$
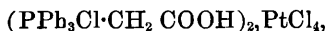
forms long, golden-yellow needles.

Triphenylphosphorcholine hydrochloride, $PPh_3Cl \cdot CH_2 \cdot CH_2 \cdot OH$, is prepared by heating ethylene chlorohydrin with triphenylphosphine. It forms white, lustrous needles or transparent tablets, melts at 129—130°, and is very readily soluble in water and alcohol, insoluble in ether. The *platinochloride* crystallises in golden-yellow needles, and melts at 222—224°.

Triphenylphosphorcholine, obtained by the action of silver oxide on the hydrochloride, is a syrup which slowly crystallises; it has a strong alkaline reaction, and absorbs carbonic anhydride from the air.

Triphenylphosphorcholine hydrobromide forms yellowish-white crystals melting at 114°. The *hydriodide* melts at 185—186°.

Trimethylene bromide also combines with the triphenylphosphine,

forming a compound of the formula $PPh_3Br \cdot C_3H_6Br$, which crystallises from alcohol in long, transparent needles, and melts at 226—228°.   The *platinochloride* is a flocculent precipitate.

<div align="right">A. H.</div>

Aromatic Boron Compounds.   By A. MICHAELIS, M. BEHRENS, J. RABINERSON, and W. GEISLER (*Ber.*, **27**, 244—262 ; compare Abstr., 1880, 395 ; 1882, 731 ; 1889, 505).—*Diphenyl borochloride*, BPh_2Cl, is obtained by the action of phenyl borochloride on mercury diphenyl, and separated from the mercuryphenyl chloride simultaneously formed, by boiling with light petroleum, the filtrate being then fractionated.   The fraction boiling at 270—271° consists chiefly of diphenyl borochloride, whilst the fraction 271—272° contains some diphenylboric acid.   The chloride is a thick, colourless liquid which fumes slightly in the air.   It is slowly converted by boiling water into *diphenylboric acid*, $BPh_2 \cdot OH$, which is a slightly yellow, crystalline mass, melts at 264—267°, and has a peculiar penetrating dill-like odour.   It gives a beautiful, green flame when ignited in the flame of a bunsen burner.

Orthotolyl borochloride, $C_6H_4Me \cdot BCl_2$, is obtained by the action of boron chloride on mercury diorthotolyl at 150—180°, and forms a thick, colourless liquid which has a pungent odour, solidifies at a low temperature, then melts at 6°, boils at 193°, and is decomposed by water with a hissing noise, with formation of *orthotolylboric acid*, $C_6H_4Me \cdot B(OH)_2$.   The latter crystallises in slender needles, melts at 160—161°, and gives with silver nitrate a yellow precipitate which quickly decomposes into toluene, boric acid, and silver oxide.   When dried over sulphuric acid, it loses water, forming *orthotolylboroxide*, $C_6H_4Me \cdot BO$.   This melts at the same temperature as the acid, and the latter is probably, therefore, converted into the oxide before it melts.

α-Naphthyl borochloride, $C_{10}H_7{}^{\alpha} \cdot BCl_2$, is obtained by the action of boron chloride on mercury di-α-naphthyl, but, as it does not distil without decomposition, could not be obtained pure.   It reacts violently with water, yielding *α-naphthylboric acid*, $C_{10}H_7{}^{\alpha} \cdot B(OH)_2$; the latter crystallises from hot water in slender, colourless needles, becomes plastic at 242°, melts at 259°, and gives with silver nitrate a precipitate, becoming first yellow and finally black, with separation of naphthalene and silver oxide.   The acid loses water over sulphuric acid, forming *α-naphthylboron oxide*, $C_{10}H_7{}^{\alpha} \cdot BO$, which is a microcrystalline powder.

β-Naphthyl borochloride is obtained from boron chloride and mercury β-dinaphthyl.   The latter is prepared in the usual manner, by treating β-bromonaphthalene with sodium amalgam in xylene solution containing ethylic acetate, and forms yellowish, nacreous plates or flat needles melting at 238°.   It has been converted into the following β-naphthylmercury derivatives ; the *chloride*, $C_{10}H_7 \cdot HgCl$, crystallising in fascicular aggregates of needles, and melting at 271° ; the *bromide*, $C_{10}H_7 \cdot HgBr$, crystallising in flat needles, and melting at 266° ; the *iodide*, $C_{10}H_7 \cdot HgI$, forms yellowish plates, melting at 251° ; the *formate*, $C_{10}H_7 \cdot Hg \cdot O \cdot CHO$, large, colourless, vitreous plates melting at

155—158°; and the *acetate*, $C_{10}H_7 \cdot Hg \cdot OAc$, flat, colourless needles melting at 147—148°.

β-Naphthyl borochloride forms colourless needles, melts at 116°, fumes in the air, and is converted by water into *β-naphthylboric acid*, $C_{10}H_7 \cdot B(OH)_2$, which exists in two modifications, the first crystallising in broad, colourless plates melting at 248°, and the second in slender needles melting at 266°. The *barium*, *silver*, and *methylic* salts have been prepared, but are only obtained with difficulty. *β-Naphthylborooxide* crystallises in colourless needles, and melts at 266°.

Attempts to obtain phenylboric acid derivatives containing a hydroxyl group in the phenyl residue were unsuccessful, but the corresponding methoxy- and ethoxy-compounds have been prepared.

Paranisyl borochloride, $OMe \cdot C_6H_4 \cdot BCl_2$, is obtained by acting on mercury diparanisyl with boron chloride at the ordinary temperature; it is a colourless liquid which becomes pale yellow to violet after a time, boils at 182° under 170 mm. pressure, solidifies on cooling, and then melts at 30°. It is violently acted on by water, with formation of *paranisylboric acid*, $OMe \cdot C_6H_4 \cdot B(OH)_2$, which crystallises from water in tabular, probably monosymmetric crystals, and melts at 201—203°. The corresponding oxide could not be obtained.

For the investigation of the orthanisyl compounds, the preparation of *mercury diorthanisyl* was necessary; it was obtained by the usual reaction, and crystallises in monosymmetric prisms melting at 108°. It yields the following mercury orthanisyl derivatives: the *chloride*, $OMe \cdot C_6H_4 \cdot HgCl$, crystallising in small needles or tablets, and melting at 173—174°; the *bromide*, $OMe \cdot C_6H_4 \cdot HgBr$, melting at 183°; the *iodide*, $OMe \cdot C_6H_4 \cdot HgI$, melting at 165°; and the *acetate*,

$$OMe \cdot C_6H_4 \cdot HgOAc,$$
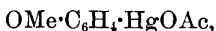
crystallising in small needles, and melting at 123—124°.

Orthanisyl borochloride, $OMe \cdot C_6H_4 \cdot BCl_2$, was not obtained pure, but yields with water *orthanisylboric acid*, $OMe \cdot C_6H_4 \cdot B(OH)_2$, which crystallises from hot water in small, lustrous plates, and melts at 165°.

The following mercury phenetyl compounds have been prepared in order to obtain the corresponding boron compounds. *Mercury diparaphenetyl*, $Hg(C_6H_4 \cdot OEt)_2$, is formed in the usual manner, crystallises in lustrous, cube-shaped crystals, melts at 135°, and has a sp. gr. of 1·0028 at 15°. It yields the following mercury paraphenetyl compounds: the *chloride*, $OEt \cdot C_6H_4 \cdot HgCl$, melting at 234°; the *bromide*, $OEt \cdot C_6H_4 \cdot HgBr$, melting at 241·5°; the *iodide*, $OEt \cdot C_6H_4 \cdot HgI$, melting at 216°; the *oxide*, $(OEt \cdot C_6H_4 \cdot Hg)_2O$, crystallising in small, white needles, and melting at 202°; the *acetate*, $OEt \cdot C_6H_4 \cdot HgOAc$, crystallising in colourless, rhombohedral tablets or stellate groups of long needles; the *propionate* melting at 116°; the *butyrate* melting at 129°; the *cyanide*, $OEt \cdot C_6H_4 \cdot HgCN$, melting at 158—159°; and the *thiocyanate* melting at 210°. *Mercury diorthophenetyl* crystallises in lustrous needles, and melts at 224°. *Mercury orthophenetyl chloride* forms lustrous needles, melting at 132°; the *bromide*, four-sided prisms, melting at 121°; the *iodide*, thick, prismatic needles, melting at 111°; the *acetate*, white plates melting at 150·5°.

p 2

Both mercury diphenetyls are converted by boron chloride at the ordinary temperature into the corresponding borochlorides which yield the analogous boric acids with water. *Paraphenetyl borochloride* is a colourless liquid, which boils at 220° under 400 mm. pressure, readily assumes a reddish colour, and forms a crystalline mass on cooling which melts again at 2°. The corresponding *paraphenetylboric acid*, $OEt \cdot C_6H_4 \cdot B(OH)_2$, crystallises in lustrous prisms or feathery aggregates of lustrous needles, and melts at 159°. *Orthophenetyl borochloride* has not been obtained pure, but yields with water *orthophenetylboric acid* which crystallises from water in small, white needles, and melts at 171°. Neither of these acids yields an anhydride.

H. G. C.

Isomerism of 1 : 3-Triketones. By L. CLAISEN (*Ber.*, **27**, 114—118).—Tribenzoylmethane, when slowly dissolved in alcoholic sodium ethoxide at 0°, and then precipitated by saturating the solution with carbonic anhydride, is obtained in an isomeric form, which is readily soluble in aqueous sodium carbonate, unlike the original substance, into which it may be reconverted by heating with alcohol. The original substance is probably $CBzO \cdot CHBz_2$, the isomeride having the tautomeric constitution $OH \cdot CBz : CBz_2$. The same explanation may be given of the isomerism of the dibenzoylacetones (dibenzoyl-acetylmethane) (this vol., i, 32). In the series $CHBz_3$, $CHBz_2Ac$, $CHBzAc_2$, $CHAc_3$, the tendency to form the more acid variety increases, $CHAc_3$, being only known in this form, which is the one readily soluble in alkaline carbonates.

C. F. B.

Synthesis of Isocoumarin and of some Derivatives of Isoquinoline. By E. BAMBERGER and W. FREW (*Ber.*, **27**, 198—212).— Isocoumarincarboxylic acid, $C_6H_4 < \genfrac{}{}{0pt}{}{CO \cdot O}{CH:C \cdot COOH}$ (*Abstr.*, 1892, 857), does not react with secondary amines, but with primary amines, NH_2R, it yields derivatives $C_6H_4 < \genfrac{}{}{0pt}{}{CO \cdot NR}{CH:C \cdot COOH}$. Aniline, ethylamine, and methylamine yield respectively *phenyl-*, *ethyl-*, and *methyl-isocarbostyrilcarboxylic acids*, as yellowish or white prisms, melting at 265°, 202°, and 238°. These substances, when heated, yield respectively *phenyl-*, *ethyl-*, and *methyl-isocarbostyril*, $C_6H_4 < \genfrac{}{}{0pt}{}{CO \cdot NR}{CH:CH}$; the first forms white needles, melting at 117·5°; the others yellowish oils, boiling at 310—311° (at 240° under 120 mm.), and 314—315° under 720 mm. pressure. The methyl compound eventually solidifies to white plates melting at 40°, and is, doubtless, identical with the substance prepared by Fernau from isoquinoline, and by Decker by oxidising isoquinoline methiodide. Methylisocarbostyril yields a *dibromide*, which forms a yellowish crystalline powder, melts at 120°, and, when boiled with water, yields *monobromomethylisocarbostyril* as needles, melting at 132°.

Isocoumarincarboxylic acid may be converted, by the dry distillation of its silver salt, into *isocoumarin*, $C_6H_4 < \genfrac{}{}{0pt}{}{CO \cdot O}{CH:CH}$, which forms

white crystals, melting at 47°, and boiling at 285—286° under 719 mm. pressure. This substance yields a *dibromide*, crystallising in pyramids, and melting at 135°, and, when heated at 120—130° with alcoholic ammonia, is converted into isocarbostyril.

When gently warmed with a solution of sodium carbonate, iso-coumarin is converted into *anhydro-orthohydroxyvinylbenzoic acid*, $O(CH:CH \cdot C_6H_4 \cdot COOH)_2$. This crystallises in tiny, white needles, melting at 183—184°, and, when heated with dilute hydrochloric acid at 150—160°, yields ·an *anhydride*, $C_6H_4 < {\text{CO}\text{——O——CO} \atop \text{CH:CH·O·CH:CH}} > C_6H_4$, as white needles, melting at 234—235°. The latter substance, when heated with alcoholic ammonia at 170°, yields the corresponding *imide*, $C_6H_4 < {\text{CO——NH——CO} \atop \text{CH:CH·O·CH:CH}} > C_6H_4$, which forms yellow crystals, melting at 285°. The anhydro-acid itself is oxidised by permanganate to phthalic acid; when fused with potash, it yields an acid, $C_{14}H_{10}(COOH)_2$, which crystallises in small, white needles and melts at 189°. The constitution of this acid has not yet been determined, but it is certainly not stilbenedicarboxylic acid, as its silver salt yields no stilbene when distilled. C. F. B.

Metaphenylenediacetic acid and the corresponding Nitrile. By G. ODDO (*Gazzetta*, **23**, ii, 336—344; compare Kipping, Trans., 1888, 42).—The *potassium* salt of metaphenylenediacetic acid crystal-lises in transparent prisms containing $7H_2O$, of which six are lost in a vacuum over sulphuric acid. The *potassium hydrogen* salt forms anhydrous scales, which melt at 231—232°. The *methylic* salt is a colourless liquid, which boils at 298—300°, and has a pleasant odour. By the action of sulphuric acid on metaphenylenediacetonitrile, a yellowish substance is produced, which contains oxygen, but whose composition could not be determined. W. J. P.

The β-Oxalkylbenzylmalonic acids. By C. LIEBERMANN (*Ber.*, **27**, 289—293; compare Abstr., 1893, i, 583).—The methylic and ethylic salts of benzalmalonic acid solidify at winter temperatures in crystals. The *methylic* salt melts at 41° and boils at 210—215° at 60 mm., whilst the ethylic salt (*Ann.*, **218**, 133) melts at 27—29°.

β-Methoxybenzylmalonic acid, $OMe \cdot CHPh \cdot CH(COOH)_2$, obtained by adding sodium methoxide to methylic benzalmalonate and decom-posing this salt with baryta water, is a white crystalline powder, which is moderately soluble in cold water, readily in alcohol, but almost insoluble in benzene. Its ethereal solution does not de-colorise bromine, and it is only oxidised by permanganate in solution in sodium carbonate after a little time. When heated, it melts at about 115°, methylic alcohol being given off and benzalmalonic acid formed, which immediately solidifies, and then melts at 197° with evolution of carbonic anhydride. This decomposition into methylic alcohol and benzalmalonic acid is quantitative at 120°. The *barium salt*, $C_{11}H_{10}O_5Ba + 2H_2O$, is precipitated almost immediately when barium chloride is added to a neutral solution of the acid in ammonia, differing in this respect from that of benzalmalonic acid.

Ethoxybenzylmalonic acid, $OEt \cdot CHPh \cdot CH(COOH)_2$, is a similar substance, and, as well as its ethereal salts, decomposes when heated with elimination of ethylic alcohol. The barium salt has been previously described by Claisen and Crismer. The behaviour of these substances as saturated compounds is used by the author as an argument, against the formula proposed by Nef (*Annalen*, 266, 68) for ethylic sodiomalonate.   A. H.

Bismuth Gallanilide. By P. CAZENEUVE (*Bull. Soc. Chim.*, 9, [3], 852—853; compare Abstr., 1893, i, 638).—*Bismuth gallanilide,* $NHPh \cdot CO \cdot C_6H_2(O_3Bi),2H_2O$, is prepared by adding a boiling aqueous solution of gallanilide (5 grams in 200 c.c.) to a solution of crystallised bismuth nitrate (15 grams) in dilute acetic acid (30 grams acid and 250 c.c. water). It is a yellow powder, which is insoluble in water and the usual solvents, and loses its water of crystallisation at 120°. The existence of this compound tends to confirm the formula $COOH \cdot C_6H_2(O_3Bi),2H_2O$, assigned by Causse (Abstr., 1893, i, 643) to basic bismuth gallate.   JN. W.

Tannin and its Estimation. By P. SISLEY (*Bull. Soc. Chim.*, [3], 9, 755—772).—The least coloured portions of dried and roughly-crushed Chinese gall nuts are extracted with cold water, the colouring matter precipitated with lead acetate, and the nearly colourless extract shaken with ether. The emulsion separates into three layers, the lowest of which consists of a syrupy solution of tannin in moist ether, having a composition represented by the formula

$$2C_{14}H_{10}O_9,7C_4H_{10}O,H_2O.$$
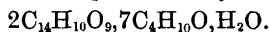
This syrup is dissolved in the minimum quantity of water, repeatedly shaken with ether to remove impurities, and the water and ether removed in a vacuum over sulphuric acid. After recrystallisation from ether, the product is pure *tannin*, a white odourless powder, soluble in all proportions of water to a clear, colourless solution, and yielding a perfectly white lead compound. The gallic acid obtained by hydrolysis of this pure material contains no trace of glucose. (For the method of estimation see this vol., ii, 169).
        JN. W.

Action of Sodium Ethoxide on Ethylic Phthalate and Ketones, and on Ethylic Phthalate and Ethylic Succinate. By E. SCHWERIN (*Ber.*, 27, 104—114).—*Acetyl-αγ-diketohydrindene,* $C_6H_4{<}^{CO}_{CO}{>}CHAc$, is prepared by heating ethylic phthalate, acetone, and sodium ethoxide in alcoholic solution on the water bath, in a reflux apparatus; the resulting sodium salt, which probably has the formula $CHNaAc \cdot CO \cdot C_6H_4 \cdot COONa$, is decomposed by carbonic anhydride, and, after purification, the hydrindene crystallises in yellow needles melting at 110°. The *phenylhydrazone,* $C_{17}H_{14}N_2O_2$, is deposited in colourless needles, melts at 184—185°, and gives an intense violet coloration with sulphuric acid and ferric chloride. The *barium salt,* $C_{11}H_8O_4Ba + H_2O$, is amorphous. *Benzoyl-αγ-diketohydrindene,* $C_6H_4{<}^{CO}_{CO}{>}CHBz$, is prepared in a similar manner from ethylic

phthalate and acetophenone, and crystallises in colourless needles, which become yellow on exposure to air, and melt at 108°. The *sodium salt*, $CHNaBz \cdot CO \cdot C_6H_4 \cdot COONa$, and the *barium salt* have also been prepared. The *trioxime* crystallises in colourless needles with $1H_2O$, darkens at 207°, and melts at 232° with decomposition. The *triphenylhydrazone* is crystalline; it darkens at about 120°, and melts at 163—167°. By the action of sodium ethoxide on the hydrindene a *sodium salt* is obtained, which probably has the formula $C_{16}H_9O_3Na + C_2H_5 \cdot OH$; it is decomposed by acids, the hydrindene being regenerated.

Propionyl-αγ-diketohydrindene, $C_6H_4 {<} {CO \atop CO} {>} CH \cdot COEt$, is formed from ethylic phthalate and ethyl methyl ketone, and crystallises in pale yellow needles melting at 103°; it sublimes on further heating, and readily dissolves in alkalis and alkaline carbonates. The *sodium salt*, $C_6H_4 {<} {CO \atop CO} {>} CNa \cdot COEt$, is deposited in yellow needles. By the action of ethylic phthalate, ethylic succinate, and sodium ethoxide, in molecular proportion, a compound is obtained which, after purification from ethylic succinosuccinate, crystallises in colourless needles; it reduces alkaline copper solution on warming, gives in alcoholic solution a greenish coloration with ferric chloride, and dissolves in alkalis. From its mode of formation and properties this substance is probably *ethylic hydronaphthaquinonecarb-oxylate*, $C_6H_4 {<} {CO \cdot CH \cdot COOEt \atop CO \cdot CH \cdot COOEt}$. The free acid could not be obtained, but, by the action of sodium ethoxide (2 mols.) on ethylic phthalate (1 mol.) and ethylic succinate (1 mol.), a compound, $C_{12}H_8O_6$, is formed, which crystallises in colourless, rhombic plates, melts at 120°, and is soluble in alkalis; on acidifying, a precipitate is obtained differing from the original substance, but it has not been further investigated. Whether either of these compounds is hydronaphthaquinonecarboxylic acid remains undetermined.　　　　J. B. T.

Derivatives of 2′-Phenylindazole.

By C. PAAL and C. LÜCKER (*Ber.*, **27**, 47 — 52; compare Abstr., 1891, 723). — 2′-Phenylindazole, $C_6H_4 {<} {N - \atop CH} {>} NPh$, is converted by oxidation with chromic acid (*Ber.*, **24**, 3058), alkaline permanganate, or dilute nitric acid into azobenzeneorthocarboxylic acid.

α-Nitrophenylindazole, $C_{13}H_9N_2 \cdot NO_2$, is obtained, together with the β-derivative, by the action of fuming nitric acid in the cold on phenylindazole. It crystallises in golden, lustrous plates, melting at 184°. When oxidised with chromic acid, it is converted into *nitro-azobenzeneorthocarboxylic acid*, $NO_2 \cdot C_{12}H_8N_2 \cdot COOH$, which crystallises from dilute alcohol in splendid red needles, melting at 135°.

β-Nitrophenylindazole forms concentric groups of small, light, yellow needles, melting at 174°.

Tribromophenylindazole, $C_{13}H_7Br_3N_2$, is the chief product obtained by boiling phenylindazole with bromine. It crystallises from acetic

acid in white needles, melting at 204°. This substance is not attacked when boiled with an acetic acid solution of chromic anhydride. *Bromophenylindazole*, $C_{13}H_9BrN_2$, is readily soluble in alcohol and acetic acid, and crystallises in small, almost white needles, melting at 147°. It appears to differ from the derivative synthetically prepared from orthonitrobenzylparabromaniline.

Phenylindazole-α-sulphonic acid, $C_{13}H_9N_2 \cdot SO_3H$, is formed, together with the β-compound, when phenylindazole is heated with fuming sulphuric acid at 120—130°. It crystallises in white, radiating needles, which are readily soluble in hot water, almost insoluble in alcohol, and blacken at about 300°. The *β-acid* is less readily soluble in water, and is formed in smaller quantity; it crystallises in small, white granules, which blacken at about 320°. The *sodium salt* of the *α-acid* forms white needles, the *barium salt* is moderately soluble in hot water, and forms elongated plates, and the *lead salt* crystallises in white, nacreous plates.

The *barium salt* of the *β-acid* is only very slightly soluble in water, and forms small granules.   A. H.

Reduction of Benziledioximes. By F. FEIST (*Ber.*, **27**, 213—215).—*Diphenylethylenediamine*, $NH_2 \cdot CHPh \cdot CHPh \cdot NH_2$, was obtained, after several unsuccessful attempts, from both α- and β-benziledioxime, by reducing them with metallic sodium in ethyl-alcoholic solution. It forms white, feathery crystals, and melts at 90—92°. The white *hydrochloride*, $C_{14}H_{16}N_2,2HCl + 2H_2O$, melts with decomposition at 248°, the yellow *picrate*, $C_{14}H_{16}N_2,2C_6H_3N_3O_7$, at 220°; the yellow *platinochloride*, $C_{14}H_{16}N_2,H_2PtCl_6 + 2H_2O$, decomposes at 222—225° without melting.   C. F. B.

Paramidotriphenylmethane. By O. FISCHER and R. ALBERT (*Ber.*, **26**, 3079—3082).—Paramidotriphenylmethane may, as already stated (Abstr., 1891, 693), be converted into the corresponding nitrile and carboxylic acid; the former is obtained by Sandmeyer's reaction, and forms vitreous prisms, which melt at 99°; it distils without decomposition, and, on hydrolysis, yields triphenylmethane-paracarboxylic acid, $CHPh_2 \cdot C_6H_4 \cdot COOH$. The latter, after repeated crystallisation from dilute acetic acid, forms white needles, and melts at 161°. The statement of Oppenheimer (Abstr., 1886, 946) that this acid melts above 350° is, therefore, incorrect. On oxidation with chromic acid in acetic acid solution, triphenylmethaneparacarboxylic acid yields the corresponding *triphenylcarbinolparacarboxylic acid*, $HO \cdot CPh_2 \cdot C_6H_4 \cdot COOH$, which crystallises in fascicular aggregates of white needles, melts at 200°, and is identical with the compound obtained by Hemilian from diphenylmethylphenylmethane (this Journal, 1875, 152).

Paramidotriphenylmethane readily undergoes condensation with aldehydes yielding crystalline compounds; the *benzylidene* derivative, $CHPh_2 \cdot C_6H_4 \cdot N{:}CHPh$, crystallises from alcohol in colourless needles, and melts at 135—136°; the *orthohydroxybenzylidene* derivative forms yellow, lustrous needles, and melts at 138°; the *paranitrobenzylidene*

and *orthonitrobenzylidene* derivatives also crystallise in yellow needles, and melt at 126—127° and 114—115° respectively.

When diazotised and treated with an alcoholic solution of β-naphthol, paramidotriphenylmethane yields an azo-colouring matter, *triphenylmethaneazo-β-naphthol*, which crystallises in long, red needles. Resorcinol and α-naphthylamine yield similar colouring matters. · H. G. C.

Constitution of Rosanilines. By A. ROSENSTIEHL (*Bull. Soc. Chim.*, [3], **9**, 833—847; compare Abstr., 1893, i, 332).— The author's recent observation of the assumption of a fourth molecule of hydrogen chloride by the di- and tri-amido-derivatives of triphenylmethane and analogous compounds (Abstr., 1893, i, 332) is of importance as tending to disprove the formula, $C_6H_4{<}{\begin{smallmatrix}C(C_6H_4\cdot NH_2)_2\\|\\NH,HCl\end{smallmatrix}}$, proposed by Fischer for pararosaniline hydrochloride, a formula containing the group, $C_6H_4{<}{\begin{smallmatrix}C=\\|\\NH\end{smallmatrix}}$, supposed to be common to all coloured substances of this class.

Miolatti's recent work on the conductivity of pararosaniline hydrochloride (Abstr., 1893, i, 572) is distinctly in favour of the present author's "ethereal salt" formula, $C(C_6H_4\cdot NH_2)_3Cl$, and against Fischer's, for the fact that the conductivity does not materially increase with dilution shows that the salt, unlike the di- and tri-hydrochlorides, is not a true electrolyte, and is, therefore, not the salt of an amine. The actual conductivity observed by Miolatti is small, and may very well be due to the action of the basic groups, since it is known from Ostwald's work that many amines are conductors.

Fischer and Jennings' recent criticism (Abstr., 1893, i, 711) of the author's formula, based on certain observations on pararosaniline hydrocyanide and hydrochloride may be turned readily against them. The hydrocyanide, admitted by them to be triamidotriphenylacetonitrile, was contrasted with the hydrochloride with the view of proving that the constitutions of the two substances must be dissimilar. It is true that the former is colourless and insoluble in water, whilst the latter is coloured and soluble; but since colour and solubility are not yet represented in chemical formula, the argument is of little weight. It is also true that the nitrile is stable, and the hydrochloride unstable, towards alkalis; but this is precisely what is to be expected from cyano- and chloro-derivatives of a substituted methane. The complex series of changes, again, which Fischer and Jennings are compelled to assume in the conversion of pararosaniline hydrochloride into triamidotriphenylcarbinol, is quite unnecessary if the author's view be taken, the action then appearing as normal, simple hydrolysis. As to rosolic and auric acids, to which Fischer and Jennings assign formulæ analogous to their rosaniline formula, it is the metallic salts which are coloured, and not the anhydrides. Sodium aurate and the corresponding hydrochloride may well be represented by the formulæ $C(C_6H_4\cdot OH)_3\cdot ONa$ and $C(C_6H_4\cdot OH)_3Cl$, thus accentuating analogies which Fischer's formulæ pass over. The anhydride

may certainly have the formula assigned to it by Nietzki, but it is not a substance in any way analogous to the others under discussion.

With regard to the contention that the assumption by pararosaniline of a fourth mol. of hydrogen chloride augments the probability of Nietzki's quinonoïd formula, it is to be observed that quinone, in taking up hydrogen chloride, loses the characteristic quinonoïd structure simultaneously with its colour.

Triamidotriphenylcarbinol and its analogues then form two classes of salts :—Ethereal salts, of which "rosaniline hydrochloride" is a type, and additive or ammonium salts, of which the di-, tri-, and tetra-hydrochlorides are types.   JN. W.

Naphthaquinone Chlorimides. By P. FRIEDLÄNDER and O. REINHARDT (*Ber.*, **27**, 238—244).—1 : 4-*Naphthaquinone chlorimide*, $O{:}C_{10}H_6{:}NCl$, is readily obtained by the action of a solution of bleaching powder on 1 : 4-amidonaphthol at 0°. It forms hair-like, yellow needles, and, after recrystallisation from alcohol or acetic acid, melts at 109·5°, and decomposes with a slight explosion at 130—133°. It slowly becomes brown at 80°, colours the skin brown, and is reconverted by stannous chloride into 1 : 4-amidonaphthol. With concentrated hydrochloric acid, it yields 2 : 3-dichloro-1 : 4-naphthaquinone, differing in this respect from quinonechlorimide, which yields dichloramidophenol or tetraphenylenediamine. Hydroxylamine converts the chlorimide into 1 : 4-nitrosonaphthol, which the authors find to melt at 193—194°.

β-Naphthaquinone-α-chloromide is obtained in a similar manner to the 1 : 4-derivative, but is much more unstable than this compound. It forms felted aggregates of slender, yellow needles, melts at 86—87°, and colours the skin brown. It dissolves in a solution of sodium hydrogen sulphite, yielding 1 : 2 : 4-*amidonaphtholsulphonic acid*, which crystallises in slender, white needles, and rapidly becomes violet when moist. The α-chlorimide yields α-nitroso-β-naphthol with hydroxylamine.

β-Naphthaquinone-β-chlorimide, prepared from 2 : 1-amidonaphthol forms brownish-yellow needles, decomposes without melting at 98', and yields with sodium hydrogen sulphite 2 : 1 : 4-amidonaphtholsulphonic acid, and with hydroxylamine, β-nitroso-α-naphthol.

All these naphthaquinone chlorimides yield resinous products with ammonia and phenylhydrazine, and, unlike quinonechlorimide, do not combine with tertiary bases to form colouring matters. Aniline converts them into quinoneanilides.

β-Naphthaquinonedichlorodiimide, $C_{10}H_6(NCl)_2$, is formed by the action of bleaching powder on 1 : 2-naphthylenediamine. It forms yellow needles, is very unstable, melts at 105°, and decomposes at 120°. It is reconverted by stannous chloride into the diamine.   H. G. C.

Action of α- and β-Naphthylamine with Nitrobenzaldehydes. By E. ZENONI (*Gazzetta*, **23**, ii, 519).—The condensation products of the nitrobenzaldehydes with the naphthylamines have the constitution $NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_{10}H_7$ in place of that indicated by the author (this vol., i, 137).   W. J. P.

1 : 2-Amidonaphthol-4-sulphonic acid. By M. BÖNIGER (*Ber.*, **27**, 23—30).—1 : 2-Amidonaphthol-4-sulphonic acid, which is identical with the compound described by Schmidt (Abstr., 1892, 476), is prepared by dissolving 1 : 2-nitrosonaphthol in cold sodium hydrogen sulphite solution, heating the liquid to 30—40°, and acidifying with hydrochloric acid. The sulphonic acid separates as a white, crystalline powder, with a faint tinge of red, and is insoluble in boiling water. When its solution in boiling, aqueous sodium hydrogen sulphite is allowed to cool, the *acid sodium salt*, $OH \cdot C_{10}H_5(NH_2) \cdot SO_3Na$, separates in faintly yellow needles, which readily become red in the light. This salt dissolves in boiling water to a small extent, and its solution has a blue fluorescence. As a photographic developer it closely resembles " eikonogen."

1 : 2-*Naphthaquinone-4-sulphonic acid* is prepared (German Patent, S. 7608) by treating the amidonaphtholsulphonic acid with $1\frac{1}{2}$ parts of nitric acid of 20 per cent., dissolving in water the ammonium salt which separates, and adding a concentrated solution of potassium chloride. The *potassium salt* is thus formed in golden-yellow needles, which deflagrate at 170—175°. When this salt is treated in aqueous solution with aniline, anilidonaphthaquinone,

$$OH \cdot C_{10}H_5O \colon NPh \ [O \colon OH \colon NPh = 1 \colon 2 \colon 4],$$
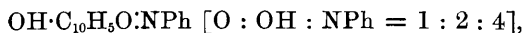
is formed ; this crystallises from alcohol in needles with a golden lustre, which melt above 240° with decomposition. When boiled with alcohol and sulphuric acid, it is converted into β-hydroxy-α-naphthaquinone, $OH \cdot C_{10}H_5O_2$, melting at 190°, its constitution and that of the amidonaphtholsulphonic acid being thus proved. Naphthaquinonesulphonic acid reacts in a similar manner with other primary amines, and also with other compounds containing the amido-group, derivatives of β-hydroxy-α-naphthaquinone being formed. The compound obtained from amidoazobenzene, $OH \cdot C_{10}H_5O \colon N \cdot C_6H_4 \cdot N_2 \cdot Ph$, is insoluble in water and dilute acids, soluble without change in dilute alkalis, and slightly soluble in alcohol, from which it crystallises in fine red needles melting, with decomposition, at about 250°. The derivative of paraphenylenediamine, $OH \cdot C_{10}H_5O \colon N \cdot C_6H_4 \cdot NH_2$, is a bluish-red precipitate which is insoluble in water, readily soluble in dilute alkalis, and slightly soluble in dilute mineral acids ; it decomposes above 280° without melting. Sulphanilic acid yields a compound of the formula $OH \cdot C_{10}H_5O \colon N \cdot C_6H_4 \cdot SO_3Na$, which crystallises in lustrous, yellowish-red plates, and, as well as the free acid, is readily soluble in water and concentrated sulphuric acid. Sodium naphthionate produces a brownish-red substance which has similar properties. Paramidodimethylaniline reacts with the naphthaquinonesulphonic acid to form a compound of the formula $OH \cdot C_{10}H_5O \colon N \cdot C_6H_4 \cdot NMe_2$, which is a derivative of β-hydroxyindophenol. It dissolves readily in dilute alkalis or acids, is insoluble in water, but soluble in alcohol, and melts and froths up at 232°. Like indophenol, it may be reduced by tin acetate to the leuco-compound $C_{10}H_5(OH)_2 \cdot NH \cdot C_6H_4 \cdot NMe_2$, which is readily soluble in acetic acid, and may be applied in calico printing, but gives colours which are destroyed by alkalis. Paramidoethylbenzylanilinesulphonic acid yields a similar derivative.

When heated with aniline and aniline hydrochloride at 120°, 1 : 2-naphthaquinonesulphonic acid is converted into anilidonaphthaquinoneanil, melting at 180°, $NHPh \cdot C_{10}H_5O \colon NPh$, and it can therefore be converted into rosindulines. The indulines prepared from potassium naphthaquinonesulphonate and the products of its reaction with paraphenylenediamine and dimethylparaphenylenediamine are readily soluble, and closely resemble the colouring matters known as paraphenylene violet, &c., obtained from paraphenylenediamine and amidoazobenzene.

1 : 2-Naphthaquinol-4-sulphonic acid is formed when the naphthaquinone compound is reduced with sulphurous acid, and has been previously obtained by the action of sodium hydrogen sulphite on β-naphthaquinone.

2 : 1-Nitrosonaphthol, when treated with bisulphite, yields the corresponding 2 : 1-*amidonaphthol-4-sulphonic acid*, which is also converted by oxidation into 1 : 2-naphthaquinone-4-sulphonic acid.   A. H.

Syntheses in the Acridine Series; 2 : 2'-Phenylamidonaphthol. By O. FISCHER and H. SCHÜTTE (*Ber.*, **26**, 3085—3089). —Nitrodiphenylmethane is slowly converted by tin and boiling hydrochloric acid into *amidodiphenylmethane*, $CH_2Ph \cdot C_6H_4 \cdot NH_2$, the *hydrochloride* of which is isolated in the usual manner, and forms colourless, nodular, crystalline aggregates melting at 175°; the free base is an oil which volatilises in a current of steam. The *acetyl* derivative crystallises in stellate groups of needles, and melts at 135°. When passed through a layer of lead oxide 15 cm. in length, heated to moderate redness, amidodiphenylmethane is converted into acridine.

When β-dinaphthylmetaphenylenediamine is fused with benzoic acid and zinc chloride, it is converted into β-*naphthalidomesophenylphenonaphthacridine*, $C_{10}H_6 \underset{CPh}{\overset{N}{<}} \!\!\! > C_6H_3 \cdot NH \cdot C_{10}H_7$, which crystallises from benzene in yellow needles melting at 244°, and gives solutions having a yellowish-green fluorescence. The salts form red colouring matters, but show no distinct fluorescence. The β-dinaphthylmetaphenylenediamine was prepared by heating β-naphthylamine and metaphenylenediamine together at 300° for some time, and melts at 192°; the compound described by Ruhemann (Abstr., 1882, 391) under this name is in reality the mononaphthyl derivative (compare Abstr., 1893, i, 420).

2 : 2'-Phenylamidonaphthol, obtained by Hepp from 2 : 2'-dihydroxynaphthalene, crystallises in small white needles, and melts at 160°. In alcoholic solution, ferric chloride gives with it a dark, flocculent precipitate, and bromine a red precipitate; it readily reduces solutions of silver salts, and has no pronounced basic properties. The hydrogen of the hydroxyl group may be readily displaced by alkyl or acidyl groups; the *acetyl* derivative forms stellate groups of white needles, and melts at 162°, the *benzoyl* derivative colourless lustrous needles melting at 137°, the *methylic ether* white, silky needles melting at 137—138°, and the *ethylic ether* stellate groups of white needles melting at 164°. Both the last-named compounds are insoluble in dilute alkalis, and show a reddish-blue fluorescence in alcoholic solution.

When heated with formic acid and zinc chloride, or benzoic chloride and zinc chloride, phenylamidonaphthol also yields acridine derivatives, but these have not as yet been obtained pure. H. G. C.

Phenolphthaleïnanilide and Orcinolphthaleïnanilide. By R. ALBERT (*Ber.*, **26**, 3077—3079).—Phenolphthaleïn, like fluoresceïn (Abstr., 1893, i, 721), is acted on by heating with a mixture of aniline and aniline hydrochloride, with formation of *phenolphthaleïnanilide*, $CO<^{C_6H_4}_{NPh}>C(C_6H_4 \cdot OH)_2$, which, after repeated recrystallisation from dilute alcohol, melts at 279°. It imparts to concentrated sulphuric acid a reddish colour, dissolves in alkalis, forming a colourless solution, and is only resolved into phenolphthaleïn and aniline with great difficulty. Its *dimethyl ether* is crystalline, and melts at 192°.

Orcinolphthaleïnanilide, $CO<^{C_6H_4}_{NPh}>C<^{C_6H_2Me(OH)}_{C_6H_2Me(OH)}>O$, is obtained in a similar manner to the foregoing compound, and crystallises from alcohol in slender white needles which melt above 300°. It forms colourless solutions in alkalis, but dissolves in concentrated sulphuric acid with a yellowish-red colour. The *dimethylic ether* also forms slender colourless needles, and remains unaltered at 300°.

H. G. C.

Camphene in Essential Oils. By J. BERTRAM and H. WALBAUM (*J. pr. Chem.*, [2], **49**, 15—19).—The authors have sought for camphene in oil of lemon, ginger oil, kerso oil (Abstr., 1891, 238), and camphor oil, by taking advantage of the ease with which it may be converted into isoborneol (this vol., i, 204). They have obtained isoborneol from the first three of these, but have not yet come to a decision with regard to camphor oil. A. G. B.

New Camphor Derivatives. By G. ODDO (*Gazzetta*, **23**, ii, 314 —335 ; compare Brühl, Abstr., 1892, 200).—*Dicamphoquinone*, $(C_{10}H_{14}O)_2$, is produced on reducing monobromocamphor with sodium in toluene solution at 90°, and then passing a rapid current of carbonic anhydride through the heated solution ; the liquid part of the product is then decanted into water, and the toluene solution distilled in a current of steam. The dicamphoquinone comes over after the toluene and camphor have distilled ; it forms lustrous, yellow, rectangular plates which melt at 129—130°, after having been heated with acetic anhydride in a sealed tube at 150°, and subsequently recrystallised from dilute alcohol. If the substance is distilled, however, or heated with acetic anhydride at 220—230°, it melts at 148—150° after recrystallisation. It has a pleasant odour, is optically inactive in solution, and is very soluble in alcohol, ether, benzene, chloroform, carbon bisulphide, or acetic acid, but only sparingly so in light petroleum. Dicamphoquinone is found to have the double molecular formula in freezing acetic acid ; but although it distils without alteration at 320°, its vapour density could not be determined in a bath of sulphur vapour, owing to decomposition. A small quantity of a *substance* which melts at 220—222° is formed during the reduction of the bromocamphor ; this is still under examination. *Dicamphoquinone-*

hydrazone, $C_{32}H_{40}N_4$, crystallises in white needles melting at 190—191°, with decomposition, and is soluble in the ordinary solvents. The corresponding oxime could not be prepared. Dicamphoquinone is readily acted on by bromine in acetic acid solution without evolution of hydrogen bromide; 4 atoms of bromine seem to be taken up, but the product is unstable, and could not be purified.

Dicamphoryl, $(C_{10}H_{15}O)_2$, is obtained on reducing dicamphoquinone with zinc dust and sulphuric acid in alcoholic solution; it forms beautiful, colourless needles or scales melting at 160—162°, and is almost odourless. Cryoscopic determinations in acetic acid solution show that it has the molecular composition given above. It does not react with phenylhydrazine or hydroxylamine, and is soluble in the ordinary organic solvents. A small proportion of *dibornyl*, $(C_{10}H_{17}O)_2$, is also formed in the above method of preparation, and is the principal product if the quinone is reduced by sodium in alcoholic solution. It crystallises in beautiful, pearly scales melting at 164—166°, reacts with acid chlorides, and is insoluble in all the ordinary organic solvents. The author concludes with a discussion of the foregoing results, and assigns possible constitutional formulæ to the new compounds prepared.   W. J. P.

Derivatives of Cyano-camphor and of Ethereal Salts of Camphocarboxylic acid. By J. MINGUIN (*Ann. Chim. Phys.*, [6], **30**, 512—547).—Nearly all the results recorded in this paper have already appeared.

β-Naphthylic cyanocampholate, $CN·CH_2·C_8H_{14}·COOC_{10}H_7$, is obtained by heating cyanocamphor with sodium and β-naphthol at 200° in a sealed tube; it forms small, transparent crystals, melts at 117°, and its specific rotatory power in toluene is $[\alpha]_D = +17·1$. When either β-naphthylic, benzylic, or phenylic cyanocampholate (compare also Abstr., 1891, 463, 464) is treated with potash, hydroxycamphocarboxylic acid is obtained, whilst from the mother liquor *cyanocampholic acid*, $CN·CH_2·C_8H_{14}·COOH$, melting at 164° (*loc. cit.*), may be separated. The *sodium* salt has a specific rotatory power in alcoholic solution, $[\alpha]_D = +52·47$, whilst the rotatory power of the barium salt in aqueous solution is $[\alpha]_D = +67·4$.

Hydroxycamphocarbamic acid, $NH_2·CO·CH_2·C_8H_{14}·COOH$, is obtained by boiling an alcoholic solution of cyanocamphor or of cyanocampholic acid with potash; it melts at 205—210°, and its specific rotation in alcoholic solution is $[\alpha]_D = +63·5°$.

When the azo-derivatives of cyanocamphor (Abstr., 1892, 1343) are boiled with alcoholic potash, *benzeneazohydroxycamphocarbamic acid*, $COOH·C_8H_{14}·CH(N_2Ph)·CO·NH_2$, is formed.   A. R. L.

Campholylic Alcohol. By G. ERRERA (*Gazzetta*, **23**, ii, 497—500; compare Abstr., 1893, i, 108).—The speed of etherification of campholylic alcohol, when heated with acetic acid at 153—155°, shows it to be a tertiary alcohol; during the heating, an unsaturated hydrocarbon, probably camphelene, is produced.   W. J. P.

Campholylamine and Camphelic Alcohol. By G. ERRERA (*Gazzetta*, **23**, ii, 500—519; compare Abstr, 1892, 1345; 1893, i, 108).—A good yield of campholylamine is obtained by distilling dicamphelylcarbamide with potash; it melts at about 43° and boils at 175·5°. The hydrochloride crystallises in the monosymmetric system, $a : b : c = 2\cdot4929 : 1 : 1\cdot8758$. $\beta = 63°\ 55'$. The *acetyl* derivative, $C_9H_7 \cdot NHAc$, is obtained as a fibrous, crystalline mass, whilst the *benzoyl* derivative forms lustrous, colourless laminæ, melting at 96—97°.

Allylcamphelylthiocarbamide, $C_3H_5 \cdot NH \cdot CS \cdot NH \cdot C_9H_{17}$, separates on boiling campholylamine with allylthiocarbimide; it crystallises in thin, silky needles melting at 79—80°, and is soluble in alcohol, benzene, or light petroleum.

Phenylcamphelylthiocarbamide, obtained in a manner similar to the preceding, crystallises in lustrous, colourless laminæ, melting at 105—106°.

Camphelylammonium camphelyldithiocarbamate,

$$C_9H_{17} \cdot NH \cdot CS \cdot SN \cdot NH_2 \cdot C_9H_{17},$$
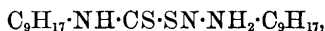
is obtained by the action of carbon bisulphide on campholylamine; heat is developed, and the salt separates in large, tabular crystals, which have an unpleasant odour and melt at 95—96°. On heating at 100°, hydrogen sulphide is evolved, and *camphelic thiocyanate*, $C_9H_{17}N \colon CS$, remains, together with campholylamine; the new salt is crystalline and melts at 24°. It has a pleasant odour, and decomposes on distillation, but is volatile in a current of steam. On heating at 100° with campholylamine, it yields dicamphelylthiocarbamide, $CS(NH \cdot C_9H_{17})_2$; it crystallises in colourless prisms melting at 108—109°, and is soluble in the ordinary solvents.

Campholylamine nitrite is obtained in colourless needles by the action of nitrous acid on the base; on heating, it breaks up, giving a mixture of *camphelene*, C_9H_{18}, and *camphelic alcohol*, $C_9H_{17} \cdot OH$. Camphelene is a colourless, mobile oil of pleasant odour, and boils at 132°; it is probably identical with the hydrocarbon obtained in the preparation of campholic chloride (Abstr., 1892, 1345). Camphelic alcohol slowly solidifies to a mass of prismatic crystals melting at 25—26°, and boils at 179—180°; it has a camphor-like odour, volatilises more readily than camphor at ordinary temperatures, and is sparingly soluble in water. Attempts to determine whether it is a primary alcohol or not, from its speed of etherification with acetic acid, were rendered futile by the readiness with which dehydration occurred and camphelene was formed. The alcohol yields a *hydrate*, $C_9H_{17} \cdot OH, \frac{1}{2}H_2O$, when shaken with water; this forms hard, prismatic crystals, melting at 36—37°. On treating the alcohol with hydrogen chloride, a mixture of *camphelic chloride*, $C_9H_{17}Cl$, and camphelene is obtained, which cannot be completely separated by distillation.

Phenylcamphelylsemicarbazide, $NHPh \cdot NH \cdot CO \cdot NH \cdot C_9H_{17}$, is prepared by mixing camphelic isocyanate and phenylhydrazine; it melts at 67—69°.

Diacetonecamphelylcarbamide, $C_9H_{17} \cdot NH \cdot CO \cdot NH \cdot CMe_2 \cdot CH_2Ac$, prepared from camphelic isocyanate and diacetonamine, crystallises in

lustrous, colourless needles, melting at 115°; it is sparingly soluble in boiling water, and yields dicamphelylcarbamide on heating above its melting point.   W. J. P.

Isoborneol. By J. BERTRAM and H. WALBAUM (*J. pr. Chem.*, [2], **49**, 1—15).—*Isoborneol*, $C_{10}H_{18}O$, is obtained by warming camphene with a mixture of acetic acid and a little sulphuric acid and decomposing the resulting acetate by alcoholic potash. It crystallises in laminæ, melts in a sealed tube at 212°, sublimes very easily, and dissolves in most organic solvents, but not in water. It is distinguished from borneol (obtained in the usual way from camphor and purified by conversion into its acetate) by its greater volatility, its higher melting point (borneol melts at 203—204° and boils at 212°), and its greater solubility in benzene and in light petroleum. At 0°, 1 part of borneol dissolves in 6·5—7 parts of benzene, and 1 part of isoborneol in 2·5—3 parts; at 20°, the solubilities become 1 in 4—4·5, and 1 in 1·5—2 respectively. At 0°, 1 part of borneol dissolves in 10—11 parts of light petroleum, and 1 part of isoborneol in 4—4·5; at 20°, the solubilities become 1 in 6, and 1 in 2·5 respectively.

The crystallography of borneol and isoborneol is given.

Isobornylphenylurethane, $C_{10}H_7O\cdot CO\cdot NHPh$, resembles bornylphenylurethane (m. p. 138—139°; Leuckart, Abstr., 1887, 376, gives 133°) in all its properties, save that, when heated with alcoholic potash, isoborneol is among the products.

The *bromal* derivative of isoborneol melts at 71—72°; the corresponding derivative of borneol melts at 98—99°. The *chloral* derivative of isoborneol does not crystallise; that of borneol melts at 55—56° (compare Abstr., 1891, 575; 1893, i, 526).

Isobornylic formate is a colourless liquid, boils at 100° (14 mm.), and is apparently identical with bornylic formate; its specific gravity is 1·017 at 15°.

Isobornylic acetate is a colourless liquid, and boils at 107° (13 mm.); its sp. gr. is 0·9905 at 15°. Bornylic acetate is crystalline, and melts at 29°, but is otherwise similar to the isobornylic salt.

Dehydrating agents convert isoborneol into camphene (m. p. 50°; b. p. 159—160°); borneol is not affected by them. With sulphuric acid and methylic and ethylic alcohols respectively, isobornylic, methylic, and ethylic ethers are obtained respectively. Borneol does not yield ethers by this treatment, but the methylic and ethylic ethers derived from it by other means do not differ in properties from those derived from isoborneol (Abstr., 1892, 200), nor is there any difference in melting point and boiling point between the methylene ethers, camphors, and camphoroximes derived from each.

The borneol of commerce is a mixture of borneol and isoborneol, and in one case consisted of 80 per cent. of the former with 20 per cent. of the latter.   A. G. B.

Santonic acid and its Derivatives. By L. FRANCESCONI (*Gazzetta*, **23**, ii, 457—468).—On oxidising santonic acid with alkaline permanganate, the author (Abstr., 1892, 1352) obtained a tetracarboxylic acid (α-acid), melting at 176°; this can be converted

into an isomeric acid (β-acid), which loses 1 mol. H_2O at 135—145°, yielding an anhydride. The α-acid has the specific rotation $[\alpha]_D = +28\cdot56°$, whilst, for the β-acid, $[\alpha]_D = 29\cdot16°$.

The *tetramethylic* salt of the α-acid, $C_{13}H_{14}O_8Me_4$, is a viscous substance, which could not be obtained crystalline; its specific rotatory power $[\alpha]_D = +56\cdot02°$. The *tetramethylic* salt of the β-acid, however, crystallises from ether in lustrous cubes melting at 99—100°, and is optically inactive. Since the α-acid can be converted into the β-isomeride, whilst the reverse change cannot be brought about, the isomerism resembles that of the substituted succinic acids and of the hydrophthalic acids.

On heating acetic acid solutions of the α-acid with iodine at 200—210°, a *dicarboxylic acid*, $C_{13}H_{14}O_8$, is obtained; it separates from its solutions in colourless crystals melting at 250—251° with decomposition, and is soluble in alcohol, ether, or boiling water. In a 3 per cent. alcoholic solution, its specific rotation $[\alpha]_D = +42\cdot8°$. The *barium* salt crystallises in long, silky needles, containing 1 mol. H_2O, which is lost at 180°. The acid is not acted on by acetic anhydride, and yields two viscid *methylic* salts, which are insoluble in sodium carbonate.

The α-acid decomposes on heating at 280—300° with caustic soda, hydrogen being evolved, and sodium carbonate, sodium acetate, and a *tricarboxylic acid*, $C_{10}H_{16}O_6$, being formed. The new acid crystallises in colourless, microscopic needles, melting at 125—126°, and is soluble in water, alcohol, or ether but only sparingly so in benzene, light petroleum, or chloroform. It is optically inactive, and yields a viscid *methylic* salt, which is also inactive and is insoluble in cold alkalis. The *barium* salt, $(C_{10}H_{13}O_6)_2Ba,2H_2O$, loses $1H_2O$ at 140—160°; the *silver* salt is obtained as a white precipitate, and is stable towards light.

If the α-acid is heated with caustic soda at 400°, a neutral *substance*, $C_8H_{14}O$, distils; this is an optically inactive, colourless oil, boiling at 169—171°, and has the normal vapour density at 205°. An oily, aliphatic *acid*, $C_6H_{12}O_2$, or $C_7H_{14}O_2$, is also obtained by heating the α-acid with soda; it boils at above 200°, and has an odour recalling that of isobutyric acid.

On treating the α-acid with red phosphorus and iodine, a *hydrocarbon*, C_8H_{16}, is obtained; it has a pleasant odour, boils at 134°, and is but slowly acted on by bromine, with evolution of hydrogen bromide. W. J. P.

New Isomerides of Santonin and Santonous acid. By A. ANDREOCCI (*Gazzetta*, **23**, ii, 468—493; compare Abstr., 1893, i, 526).—*Desmotroposantoninic acid*, $C_{15}H_{20}O_4$, is prepared by dissolving desmotroposantonin or its lactone in barium hydroxide, and extracting with ether after acidification; it can be obtained crystalline but soon changes into the lactone. The *barium* salt was prepared.

Methylic desmotroposantonite, $OH\cdot C_{14}H_{18}\cdot COOMe$, is prepared in the usual way and crystallises in needles or plates melting at 95—96°. On heating it in a reflux apparatus with methylic alcohol, methylic iodide, and sodium, under two atmospheres pressure, *methylic methyl-*

desmotroposantonite, $OMe \cdot C_{14}H_{18} \cdot COOMe$, is obtained. It is a colourless, viscous liquid, which solidifies to a vitreous mass in a freezing mixture, and boils at 300—305° under 80 mm. pressure. *Methyl-desmotroposantonous acid*, $OMe \cdot C_{14}H_{18} \cdot COOH$, is prepared by dissolving its methylic salt in methylic alcohol, adding soda, saturating with carbonic anhydride, and precipitating with sulphuric acid. It crystallises in small, white prisms melting at 97—98°, and is soluble in ether, alcohol, or light petroleum. *Ethylic desmotroposantonite* is obtained as a viscid oil.

On fusing desmotroposantonous acid with potash, it decomposes quantitatively into hydrogen, propionic acid, and 1 : 2 : 4-dimethyl-β-naphthol.

Isodesmotroposantonin, $C_{15}H_{18}O_3$, an isomeride of desmotroposantonin, is obtained by fusing the latter with potash at 210—220° ; it separates on treating the aqueous solution of the fused product with acid, and crystallises in needles melting at 187—188° with slight decomposition. It is soluble in alcohol or acetic acid, but only sparingly so in ether or hot water, and has the specific rotatory power $[\alpha]_D = +127°$ 55' in a 1·3 per cent. alcoholic solution. The *acetyl* derivative, $C_{15}H_{17}AcO_3$, is obtained in small, transparent prisms melting at 154°, and has the specific rotation $[\alpha]_D = +122°$ 36' in a 1·3 per cent. alcoholic solution.

Isodesmotroposantoninic acid, $OH \cdot C_{14}H_{18}O \cdot COOH$, is obtained by dissolving isodesmotroposantonin in barium hydroxide. It crystallises in microscopic, white needles, and soon changes into the lactone. The *barium* salt is crystalline and very soluble in water.

Lævosantonous acid is obtained by reducing isodesmotroposantonin with zinc dust and acetic acid ; it crystallises in needles melting at 176—177°, and has the specific rotation $[\alpha]_D = -74°$ 30'. On crystallising together equal weights of santonous and lævosantonous acids the inactive isosantonous acid prepared by Cannizzaro and Carnelutti is obtained ; the latter acid, which melts at 153—158°, is therefore the racemic form of the two former ones. *Ethylic lævosantonite* has the specific rotation $[\alpha]_D = -70°$ 37' ; like ethylic isosantonite, it melts at 116—117°. The racemic modification, which was prepared by Cannizzaro (*Gazzetta*, **12**, 401), is completely dissociated in freezing acetic acid. The *methylic* salt of the new acid melts at 82°, whilst methylic isosantonite melts at 81—84°.

The author is continuing the investigation of these substances.

W. J. P.

Chionanthin. By W. v. SCHULZ (*Chem. Centr.*, 1893, ii, 820—821, and 866—867 ; from *Pharm. Zeit. Russ.*, **32**, 579—581 and 593—595).—This glucoside, $C_{22}H_{28}O_{10} + 2H_2O$, was isolated from the root-bark of the Virginian snowflake shrub (*Chionanthus virginica*). It crystallises in silky, white spangles, which lose their water of crystallisation at 110°, and, at a higher temperature, turn reddish-violet, and melt to a transparent, glassy mass. Dilute acids hydrolyse it to dextrose and a reddish-brown resinous substance, which melts below 110°. It does not seem very poisonous, and its properties generally differ from those of saponin.   C F. B.

Chrysin. By G. DARIER (*Ber.*, **27**, 21—22).—The author has confirmed the results obtained by Kostanecki (this vol., i, 93) in the examination of the acetyl compound of tectochrysin, and has also studied the action of nitric acid on chrysin. *Dinitrochrysin*, $C_{15}H_8O_4(NO_2)_2$, is obtained by boiling chrysin with nitric acid of sp. gr. 1·35. It crystallises from alcohol in rose-red plates, which are only very slightly soluble in water, rather more freely in alcohol, and melt at 272° (uncorr.). When treated with acetic anhydride it is converted into *diacetyldinitrochrysin*, $C_{15}H_6O_2(NO_2)_2(OAc)_2$, which crystallises from benzene in yellow needles and melts at 229° (uncorr.). The dinitro-compound forms a yellow crystalline *potassium salt*, $C_{15}H_6O_2(NO_2)_2(OK)_2 + H_2O$, and a *calcium salt*, of the formula $C_{15}H_6O_2(NO_2)_2(O_2Ca)$. The composition of these substances may be regarded as a further proof of the existence of two hydroxyl groups in chrysin. A. H.

Action of Benzaldehyde on Symmetrical Trimethylpyridine.

By H. DUBKE (*Ber.*, **27**, 79—86).—2 : 4-*Dimethyl-α-stilbazole*,

$$C_5NH_2Me_2 \cdot CH:CHPh,$$
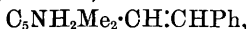
is prepared by heating trimethylpyridine with benzaldehyde and zinc chloride for six hours at 137—140°; after purification it is separated from 2:4-dimethylpyridylmethylenephenylalkine (see below) by means of mercuric chloride, and forms a yellowish-brown syrup which boils, with slight decomposition, at 188—189° under a pressure of 9 mm. The *hydrochloride* crystallises in prisms with $2H_2O$, softens at 208°, and melts at 215—217°. The *hydrobromide*, with $2H_2O$, forms slender, yellow needles melting at 218—220°. The *nitrate* crystallises in slender, colourless needles with $2H_2O$, and melts at 95—105°. The *mercurochloride*, $C_{15}H_{15}N,HgHCl_3 + H_2O$, is almost insoluble in water; it forms slender, yellow needles, softens at 208°, and melts at 218—219° with decomposition. The *aurochloride* crystallises in anhydrous needles and melts at 189—191°. The *platinochloride* forms yellowish-red needles, which melt at 230—232° with previous blackening at 220°. The *picrate* is crystalline, blackens at 230°, and melts at 240—241° with decomposition. On treatment of the base with bromine in carbon bisulphide solution, hydrogen bromide is evolved, and three compounds containing bromine are formed; they are crystalline, and melt at 213—214°, 167—168°, and 200° respectively. On reduction with sodium in alcoholic solution, the 2 : 4-dimethyl-α-stilbazole yields 2 : 4-*dimethyl-α-stilbazoline*, $C_5NH_8Me_2 \cdot CH_2 \cdot CH_2Ph$, in small quantity; it is an oily liquid and forms a crystalline *hydrochloride*, which melts at 160°—162° with decomposition. 2 : 4-*dimethylpyridylmethylenephenylalkine*, $C_5H_2NMe_2 \cdot CH_2 \cdot CHPh \cdot OH$ (see above), is a greenish-yellow, fluorescent, oily liquid, boiling, with partial decomposition, between 50° and 148° under 9 mm. pressure. The *hydrochloride* crystallises with $\frac{1}{2}$ mol. H_2O, and melts at 209—211°. The *hydrobromide* is deposited in slender, colourless, anhydrous crystals, melting at 187—188°. The *mercurochloride* and *aurochloride* each crystallise with $1H_2O$ and melt at 99—101° and 138—140° respectively. The *platinochloride*, $(C_{15}H_{17}NO)_2,H_2PtCl_6 + 2H_2O$, forms yellowish-red crystals, which melt at 125—130° with previous soften-

ing at 105°. The *picrate* crystallises in slender needles and melts at 124—125°.   J. B. T.

Action of Chloral on Aldehydecollidine. By P. SCHUBERT (*Ber.*, **27**, 86—90).—*β-Ethylpyridyl-α-trichlorohydroxypropane*,
$$C_5NH_3Et\cdot CH_2\cdot CH(OH)\cdot CCl_3,$$
is prepared by heating collidine with chloral in presence of amylic acetate for six hours at 140—150°; it is purified by means of the hydrochloride, and crystallises from alcohol, on the addition of water, in colourless plates melting at 86°. The *hydrochloride*, $C_{10}H_{12}Cl_3O,HCl$, forms transparent prisms, melting at 175—176° with decomposition. The *hydrobromide* is deposited in yellow prisms which darken at 185° and melt at 188°. The *hydriodide* is unstable, forms prismatic plates, and melts at 174°. The *platinochloride* crystallises in pale yellow plates melting at 208°. The *picrate* is deposited in yellow needles and melts at 150°. The *dichromate* crystallises in bronze plates and explodes violently at 118°. The *aurochloride* and *mercurochloride* are oily.

By the action of potassium carbonate on the base, *α-ethylpyridyl-β-lactic acid*, $C_5NH_3Et\cdot CH_2\cdot CH(OH)\cdot COOH$, is formed, and crystallises from a mixture of chloroform and light petroleum in small, lustrous plates melting at 66°. The *hydrochloride* is syrupy; the *aurochloride* crystallises with $1H_2O$, and melts at 83—84°. The *calcium salt*, $(C_{10}H_{12}NO_3)_2Ca + 4\frac{1}{2}H_2O$, is deposited in plates melting at 105° with previous softening at 100°. The *strontium salt* is anhydrous and crystalline, and melts at 143—144°. The *barium, zinc,* and *copper salts* have also been prepared ; the first two are gelatinous, the last sparingly soluble.

On heating ethylpyridyltrichlorohydroxypropane with alcoholic potash, the water is eliminated and *ethylpyridylacrylic acid*, $C_5NH_3Et\cdot CH\!:\!CH\cdot COOH$, is formed ; it crystallises from water in stellate needles, melts at 137°, and readily dissolves in sodium carbonate. The *hydrochloride* is deposited in broad plates melting at 195—197° with decomposition and previous blackening at 170°. The *aurochloride* forms prisms melting at 98°. The *mercurochloride* crystallises in pale yellow plates and melts at 142°.   J. B. T.

Resolution of β-Pipecoline and Tetrahydroquinaldine into their Optical Isomerides. By A. LADENBURG (*Ber.*, **27**, 75—78).—β-Pipecoline is converted into the *hydrogen tartarate* and the salt recrystallised seven times at ordinary temperatures ; it forms hemimorphous monoclinic crystals, $a : b : c = 1\cdot27403 : 1 : 0\cdot73645$; $\beta = 98° 18'$, and melts at 170—172°. The active *base* boils at 124°, and the refractive power $[\alpha]_D = -3\cdot98°$ at 25°. These figures are approximate only, as the base was obtained in very small quantity. Tetrahydroquinaldine boils at 250° (corr.), its sp. gr. $= 1\cdot042$ at 16°/4°. The *hydrogen tartarate* forms hemimorphous, monoclinic crystals, $a : b : c = 1\cdot37956 : 1 : 1\cdot05254$; $\beta = 118° 38'$. The refractive power of the free *base* $[\alpha]_D = 55° 99'$ at 16°.   J. B. T.

Methyltetrahydroisoquinoline Methiodide. By A. FERRATINI (*Gazzetta*, **23**, ii, 409—415).—The oily base which the author has

previously obtained (Abstr., 1893, i, 227) by distilling methyltetrahydroisoquinoline with potash is most probably *orthovinyldimethylbenzylamine*, $CH_2:CH \cdot C_6H_4 \cdot CH_2 \cdot NMe_2$. On treating its carbon bisulphide solution with bromine, it yields a crystalline *hydrobromide*, $C_{11}H_{14}NBr_3,HBr$, which melts at 108°; a small quantity of a second white, crystalline *substance*, which melts at 186°, is also obtained. The methiodide gives off trimethylamine and carbonises on heating, thus behaving in the same way as Freund's methylhydrohydrastine methiodide (Abstr., 1893, i, 116) which it resembles in constitution. Trimethylamine is also evolved on distilling the methiodide with potash. On shaking the methiodide in aqueous solution with freshly precipitated silver chloride, a crystalline *hydrochloride* is obtained which yields a yellow, crystalline *platinochloride* of the composition $(C_{12}H_{17}N)_2,H_2PtCl_6$; it melts at 224° with decomposition. The *aurochloride* melts at 159—161°, and the *picrate* is crystalline and melts at 156—159°. The *hydroxide* is obtained as a syrupy liquid, which absorbs carbonic anhydride from the air. W. J. P.

Action of Sulphur Chloride on Acetylacetone. By F. MAGNANI (*Gazzetta*, **23**, ii, 415—419).

—Sulphur chloride readily acts on acetylacetone with evolution of hydrogen chloride and development of heat. The product, which solidifies on pouring it into water, consists of *dithiodiacetylacetone*, $CHAc_2 \cdot S \cdot S \cdot CHAc_2$; it crystallises in yellowish laminæ which melt at 89—90°, and has the normal molecular weight in boiling benzene. On boiling its alcoholic solution with hydroxylamine hydrochloride, it yields a *diisooxazole*,

$$\begin{matrix} N\!:\!CMe \\ | \\ O \cdot CMe \end{matrix} \!>\! C \cdot S_2 \cdot C \!<\! \begin{matrix} CMe\!:\!N \\ | \\ CMe \cdot O \end{matrix},$$

which separates from light petroleum in white needles melting at 77—78°. On treating the thioacetone with phenylhydrazine a *dipyrazole*,

$$\begin{matrix} N \,\rule[0.5ex]{1.2em}{0.4pt}\, CMe \\ | \\ NPh \cdot CMe \end{matrix} \!>\! C \cdot S_2 \cdot C \!<\! \begin{matrix} CMe \,\rule[0.5ex]{1.2em}{0.4pt}\, N \\ | \\ CMe \,\rule[0.5ex]{1.2em}{0.4pt}\, NPh \end{matrix},$$

is obtained, which crystallises in needles melting at 78—79°.

Small quantities of another *thio-derivative*, $C_{10}H_{14}O_4S_3$, which melts at 129°, are also formed during the interaction of sulphur chloride and acetylacetone. W. J. P.

Action of Halogenated Ketones on Thiocarbamides and on Ammonium Thiocarbamate. By G. MARCHESINI (*Gazzetta*, **23**, ii, 437—443; compare Spica and Carrara, Abstr., 1892, 215; Mazzara, Abstr., 1893, i, 411).

2 : 5-*Phenyldibenzileamidothiazole*,

$$\begin{matrix} CH \cdot S \\ \| \\ CPh \cdot N \end{matrix} \!\!\gg\! C \cdot N(C_7H_7)_2,$$
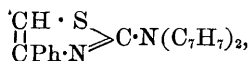
is prepared by heating unsymmetrical dibenzilethiocarbamide and bromacetophenone with acetone in a reflux apparatus; it crystallises in white needles melting at 106°, is soluble in alcohol or ether but not in water. On treatment with potash, it yields a *substance* which is soluble in ether, and melts at 85—86°.

On heating symmetrical dibenzilethiocarbamide with bromacetophenone, 1 : 2 : 5-*benzilephenylbenzileimidothiazoline*,

$$\begin{matrix} \text{CH}\text{------}\text{S} \\ \text{CPh·N(C}_7\text{H}_7) \end{matrix} > \text{C:N·C}_7\text{H}_7,$$

and its *hydrobromide*, $C_{23}H_{20}N_2S,HBr$, are obtained. The base crystallises in needles melting at 66—67°, and is soluble in water, alcohol, or ether. The hydrobromide forms large, colourless, transparent, monosymmetric crystals which melt at 173°; it is very soluble in alcohol, but sparingly so in water.

Ammonium thiocarbamate acts on chloracetone in boiling alcoholic solution with formation of 2 : 5-methylhydroxythiazole (compare Tscherniac, Abstr., 1892, 1425).   W. J. P.

Syntheses of Quinazolines. By C. PAAL, W. KRÜCKEBERG, F. KOCH, S. KÜTTNER, A. NEUBURGER, and K. STOLLBERG (*J. pr. Chem.*, [2], **48**, 537—575; compare Abstr., 1890, 1443; 1892, 80; 1893, i, 438).—*Orthonitrobenzylparachloraniline*, $NO_2·C_6H_4·CH_2·NH·C_6H_4Cl$, from orthonitrobenzylic chloride and parachloraniline, crystallises in yellow prisms, melts at 85°, and dissolves in the usual organic solvents, but not in water (compare Abstr., 1891, 723). When heated with formic acid, it yields *orthonitrobenzylparachloroformanilide*,

$$NO_2·C_6H_4·CH_2·N(C_6H_4Cl)·CHO,$$

which crystallises in colourless needles, melts at 110°, and is sparingly soluble in organic solvents.

3'-Parachlorophenyldihydroquinazoline, $C_6H_4 \begin{smallmatrix} N=CH \\ CH_2·N·C_6H_4Cl \end{smallmatrix}$, is prepared by reducing the formanilide ; it crystallises in white needles or laminæ, melts at 143°, and dissolves in most organic solvents and in warm mineral acids. The *stannochloride* (m. p. 189°), *hydrochloride*, *platinochloride* (m. p. 317°), *zincochloride* (m. p. 89°), *nitrate* (m. p. 156°), *acid sulphate* (m. p. 185°), *acid oxalate* (m. p. 168°), and *picrate* (m. p. 192°) are described.

3'-Parachlorophenyl-4'-ketodihydroquinazoline, $C_6H_4 \begin{smallmatrix} N=CH \\ CO·N·C_6H_4Cl \end{smallmatrix}$, is prepared from the preceding compound by oxidation with alkaline potassium permanganate. It crystallises in pale yellow, thin, stellate needles, melts at 177°, and dissolves in most organic solvents, but not in water. The *hydrochloride* melts at 192°, the *platinochloride* at 315°. By reduction with sodium, 3'-parachlorophenyldihydroquinazoline yields phenyltetrahydroquinazoline.

Orthamidobenzylparabromaniline, prepared by reducing the nitro-derivative (Abstr., 1893, 438) with zinc dust and acetic acid, crystallises in nearly white needles, melts at 104°, and dissolves in most organic solvents and mineral acids. When heated with formic acid, it yields *orthonitrobenzylparabromoformanilide*, which crystallises in colourless prisms, melts at 105°, and dissolves sparingly in the usual solvents. When reduced with tin and hydrochloric acid, the formanilide yields *3'-parabromophenyldihydroquinazoline*, which crystallises in white laminæ or flat needles, melts at 142°, and is sparingly soluble in light petroleum, but freely soluble in hot alcohol ; the *hydrochloride*, *platinochloride*, *aurochloride*, *acid oxalate*, and *picrate* (m. p. 202°) are described. The oxidation of the dihydroquinazoline with potassium

permanganate yields 3'-*parabromophenyl*-4'-*ketodihydroquinazoline*; this crystallises in large, pale yellow needles, melts at 174°, and dissolves sparingly in ether and light petroleum, but freely in alcohol, benzene, and glacial acetic acid; reduction with sodium converts it into 3'-phenyltetrahydroquinazoline.

Orthonitrobenzylparaphenetidine, $NO_2 \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot OEt$, from orthonitrobenzylic chloride and paraphenetidine, crystallises in large, red tables, melts at 52°, and is freely soluble in hot organic solvents, except light petroleum; by reduction with tin and hydrochloric acid, it yields 2'-paraphenetylindazole (Abstr., 1891, 724). The *hydrochloride* crystallises in needles and melts at 163°. When heated with formic acid, it yields *orthonitrobenzylformylparaphenetidine*,

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot N(C_6H_4 \cdot OEt) \cdot CHO,$$
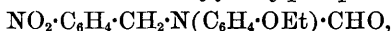
which crystallises in colourless pyramids and tables, and melts at 96°.

3'-*Paraphenetyldihydroquinazoline*, $C_6H_4 {<} {\overset{N = CH}{\underset{CH_2 \cdot N \cdot C_6H_4 \cdot OEt}{|}}}$, is obtained by reducing the above described formyl derivative; it crystallises in thin tables, melts at 109°, and dissolves in most solvents, except water and light petroleum. The *hydrochloride* (m. p. 207°), *stannochloride* (m. p. 132°), *platinochloride* (m. p. 206°), *aurochloride* (m. p. 179°), *acid oxalate* (with $1H_2O$; m. p., when anhydrous, 162°), and *picrate* (m. p. 194°) are described. The *keto*-base,

$$C_6H_4 {<} {\overset{N = CH}{\underset{CO \cdot N \cdot C_6H_4 \cdot OEt}{|}}},$$
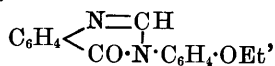
obtained by oxidising the quinazoline, crystallises in laminæ, and melts at 154°.

3'-*Paraphenetyltetrahydroquinazoline* is obtained by hydrogenating the dihydroquinazoline by sodium in alcohol; it crystallises in nacreous laminæ, and melts at 124°.

Orthonitrobenzylmetanitraniline, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot NO_2$, from orthonitrobenzylic chloride and metanitraniline, crystallises in yellow needles or laminæ, melts at 142—143°, and dissolves in most solvents except water and light petroleum. By treatment with formic acid, it yields *orthonitrobenzylformylmetanitraniline*,

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot N(C_6H_4 \cdot NO_2) \cdot CHO,$$
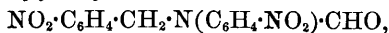
which crystallises in grey prisms, melts at 140°, and dissolves sparingly in alcohol, ethylic acetate, and benzene, but more freely in glacial acetic acid, amylic alcohol, and chloroform. The corresponding *amidophenyldihydroquinazoline*, $C_6H_4 {<} {\overset{N = CH}{\underset{CH_2 \cdot N \cdot C_6H_4 \cdot NH_2}{|}}}$, crystallises in white laminæ, melts at 147°, and becomes brown by oxidation in air; its *hydrochloride* (m. p. 230—232°), *stannochloride* (m. p. 264°), *platinochloride*, which melts with decomposition at 240°, *aurochloride*, *oxalate* (m. p. 157—159°), and *picrate* (m. p. 189°) are described; the *benzoyl*-derivative, $C_6H_7N_2 \cdot C_6H_4 \cdot NH \cdot COPh$, obtained by heating the dihydroquinazoline with benzoic chloride, is a crystalline powder, and melts at 82°. When the dihydroquinazoline is heated with methylic iodide in methylic alcohol, *metamethylamidophenyldihydroquinazoline methiodide*,

$C_6H_4<^{NMeI \cdot CH}_{CH_2-N \cdot C_6H_4 \cdot NHMe}$, separates as a hydriodide in the form of stellate crystals which melt at 153°; the free *base* crystallises in small prisms, and melts at 185°.

Metamidophenyltetrahydroquinazoline, $C_6H_4<^{NH \cdot CH_2}_{CH_2 \cdot N \cdot C_6H_4 \cdot NH_2}$, obtained by hydrogenating the dihydroquinazoline, crystallises in laminæ, and melts at 156°; its *hydrochloride*, which melts with decomposition at 210°, *stannochloride, platinochloride,* and *aurochloride* are described.

Orthonitrobenzylallylamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH:CH_2$, from orthonitrobenzylic chloride and allylamine, is a colourless oil, soluble in most organic solvents and in mineral acids; it cannot be distilled. Its *hydrochloride* (m. p. 136—137°) and *platinochloride* (m. p. 163°) are described. When heated with formic acid, it yields *orthonitrobenzylformallylamine*, a viscid, yellow oil, which cannot be distilled, and dissolves in organic solvents and concentrated mineral acids. By reduction the base yields 3'-*allyldihydroquinazoline,* a bitter, yellowish oil, having the odour of coniine, and boiling with decomposition at 280—290°; its *hydrochloride* (m. p. 165°), *hydrobromide* (m. p. 168°), *perbromide, hydriodide* (m. p. 199°), *platinochloride* (m. p. 191—192°), *acid oxalate* (m. p. 172°), and *picrate* (m. p. 172—173°) are described. The *tetrahydroquinazoline* is a colourless, easily oxidised oil, which boils at 270—272°; its *acid oxalate* melts at 164°. A. G. B.

Action of Hydrocyanic acid on Phenylhydrazine.

By E. FISCHER and F. MÜLLER (*Ber.*, **27**, 185—187).—The compound obtained by the author (*Ber.*, **22**, 1933) by warming phenylhydrazine with hydrocyanic acid is found to be identical with the cyanophenylhydrazine, $(C_7H_8N_3)_2$, described by Senf. The authors have prepared from it bisphenylmethyltriazole, bisphenylethyltriazole, and bisphenylpropyltriazole, as described by Bladin.

Bisphenyltriazole, $^{CH:N}_{NPh \cdot N}{>}C \cdot C{<}^{N:CH}_{N \cdot NPh}$, is obtained by heating cyanophenylhydrazine with formic acid. It melts at 277—278° (corr.) and dissolves in hot dilute and concentrated mineral acids.

E. C. R.

Adenine and Hypoxanthine.

By M. KRÜGER (*Zeit. physiol. Chem.*, **18**, 423—458, 459—472).—In continuation of previous work (Abstr., 1892, 219, 890; 1893, 736), the properties of a number of other preparations from adenine and hypoxanthine are described. In the first of the present papers the method of preparation, analysis, metallic compounds, solubilities, crystalline form, reactions, and decomposition products of the following substances are given :—Benzyladenine, $C_5H_4N_5 \cdot C_7H_7$; *dibenzyladenine,* $C_5H_3N_5(C_7H_7)_2$, melting at 171°; methyladenine methiodide, an additive product; *lead adenine,* $C_5H_3N_5Pb$; *diethylhypoxanthine ethiodide; methyladenine; dimethylhypoxanthine; ethyladenine; isoamyladenine* melting at 148—150°; and *isoamylhypoxanthine.*

Bromohypoxanthine can be obtained in a similar way to the corresponding adenine compound.

The second paper treats of the constitution of the adenine and hypoxanthine molecules. It is pointed out that adenine, like xanthine, guanine, and caffeïne, gives a monobromo-derivative, the hydrobromide of which will combine with four extra atoms of bromine. Hypoxanthine has the same property. The existence of dimethylhypoxanthine, which agrees in all its properties with caffeïne, shows that hypoxanthine and adenine contain two imido-groups replaceable by metals and alkyls. Adenine contains, indeed, a third imido-group, corresponding with the oxygen atom of hypoxanthine. By the oxidation of bromadenine and bromohypoxanthine with hydrochloric acid and potassium chlorate, alloxan, and large quantities of urea are produced. Hence adenine and hypoxanthine contain an alloxan nucleus ; whether a carbamide nucleus is present in addition is doubtful. On decomposing hypoxanthine and adenine by concentrated hydrochloric acid, these products are obtained qualitatively in the same way as by the decomposition of xanthine and uric acid.

By the action of concentrated hydrochloric acid on methyladenine, the methyl group is eliminated as methylamine. By the same treatment, dimethylhypoxanthine yields methylamine and methylglycocine. From these and other considerations of similar nature, the following constitutional formulæ are suggested :—

$$\begin{array}{c}NH \cdot CH:C \cdot NH \\ CH:N - C = N\end{array}\!\!>CO.$$
Hypoxanthine.

$$\begin{array}{c}NH \cdot CH:C \cdot NH \\ CH:N - C = N\end{array}\!\!>C:NH.$$
Adenine.

$$\begin{array}{c}NMe \cdot CH:C \cdot NMe \\ CH:N - C = N\end{array}\!\!>CO.$$
Dimethylhypoxanthine.

$$\begin{array}{c}NMe \cdot CH:C \cdot NH \\ CH:N - C = N\end{array}\!\!>C:NH.$$
Methyladenine.

$$\begin{array}{c}NH \cdot CBr:C \cdot NH \\ CH:N - C = N\end{array}\!\!>CO.$$
Bromohypoxanthine.

$$\begin{array}{c}NH \cdot CBr:C \cdot NH \\ CH:N - C = N\end{array}\!\!>C:NH.$$
Bromadenine.
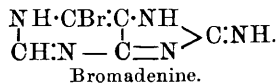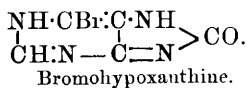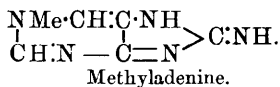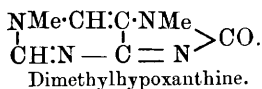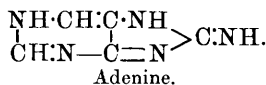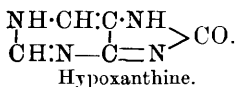
W. D. H.

Isoconiïne. By A. LADENBURG (*Bull. Soc. Chim.*, [3], **9**, 801—802 ; compare Abstr., 1893, i, 442).—Attempts to split hydroquinoline, a substance containing "asymmetric nitrogen" (*loc. cit.*), but not asymmetric carbon, into optically active modifications by fractional crystallisation of the tartrate have proved unsuccessful. This is a strong argument against the "asymmetric nitrogen" hypothesis, a point which Simon, in a critical abstract of the former paper, has contested.   JN. W.

Some New Tropeïnes. By A. PETIT and M. POLONOVSKY (*J. Pharm.*, [5], **28**, 529—531).—In some cases alkyl salts can be substituted with advantage for the corresponding acids in the preparation of tropeïnes by Ladenburg's method.

Benzilotropeïne, $C_8H_{14}NO\cdot CO\cdot CPh_2OH$, crystallises in hard prisms. It is soluble in alcohol or ether, slightly soluble in water, and is not hygroscopic. It is a strong base with a bitter taste and yields stable, crystalline salts.

Phenylcarbamotropeïne, $C_8H_{14}NO\cdot CO\cdot NHPh$, is produced by heating phenylic isocyanate with a solution of tropine in benzene on the water bath for some minutes. Diphenylcarbamide is formed in small quantity at the same time. This urethane is insoluble in water, sparingly soluble in cold benzene, and soluble in alcohol or ether. Its hydrochloride is precipitated by an excess of acid.

Succinotropeïne is obtained as an oil. Its aurochloride crystallises in yellow needles melting at 167°. W. T.

Caffearine. By P. PALLADINO (*Chem. Centr.*, 1893, ii, 721; from *Apoth. Zeit.*, **8**, 443—444).—This alkaloïd was obtained by a lengthy process from coffee, and crystallises in needles readily soluble in water and alcohol. The *hydrochloride*, $C_{14}H_{16}N_2O_4,HCl + H_2O$, also crystallises in needles. C. F. B.

Nucleïc acid. By A. KOSSEL (*Chem. Centr.*, 1893, ii, 649—650; from *Centr. Med. Wiss.*, 1893, 497—499).—The author replies to Liebermann and v. Bittó (see this vol., i, 155), that their analysis of the baryta precipitate does not fulfil the requirements of a scientific research either in its execution or in its results. The author also points out that he has not in any particular adopted the views of Liebermann as to the nucleïns. The two views are, in fact, fundamentally different. Liebermann's observations on the formation of xanthine substances do not in any way affect Kossel's view that the nucleïn bases are formed by the decomposition of the molecule of nucleïn or nucleic acid. A. H.

Albumin of the Hen's Egg. By E. SALKOWSKI (*Chem. Centr.*, 1893, ii, 532; from *Centr. med. Wiss.*, **31**, 513—515).—If a solution of hen's egg albumin is carefully neutralised with dilute acetic acid, and the solution precipitated by boiling, a hitherto unobserved albumose is found in the filtrate. The latter is isolated by concentrating the solution and precipitating with absolute alcohol. It is readily soluble in water, gives the biuret reaction, is precipitated by ammonium sulphate, tannin, and a hydrochloric acid solution of phosphotungstic acid, but not by acetic acid or sodium chloride. When the solution is evaporated on the water bath, it passes into an insoluble anhydride which swells up in water and is insoluble in dilute acids, concentrated hydrochloric acid, and glacial acetic acid. The anhydride dissolves in nitric acid of sp. gr. 1·2, with a yellow colour which changes to orange on the addition of alkali. It swells up in dilute ammonia, partially dissolving at the same time; it dissolves readily in dilute aqueous soda, and is not precipitated from the solution by acetic acid. The fermentable sugar which the albumin contains is glucose. H. G. C.

Constitution of Vegetable Proteïds. By E. FLEURENT (*Compt. rend.*, **117**, 790—793).—Gluten, gluten-caseïn, gluten-fibrin, legumin,

and vegetable albumin were heated with barium hydroxide solution, as in Schützenberger's experiments with proteïds of animal origin. The products are qualitatively the same, and the non-volatile products likewise amount to about 95 per cent. of the original substance, but the ratio of the ammonia to the barium oxalate and carbonate is very different. In the case of proteïds of the gluten group it is higher, and in the case of legumin and vegetable albumin it is lower, than with proteïds of animal origin. Vegetable caseïn and vegetable fibrin give identical results.

It is known that the splitting up of gluten yields glutamic acid, whilst legumin and vegetable albumin yield aspartic acid, and it would seem that, as Schützenberger suggests, the disproportion between the ammonia and the insoluble barium salts is due to the existence of an amide similar to asparagine in the molecule of the vegetable proteïd. Glutamic and aspartic acids are liberated and afterwards decompose, yielding a further quantity of barium carbonate. This view is supported by the fact that in the case of gluten the proportions of ammonia and oxalic acid remain constant, but the proportion of barium carbonate increases with the duration of the reaction. The same phenomenon is observed in the case of vegetable albumin and legumin. In the fixed residue, the ratio of carbon to hydrogen, C_nH_{2n}. is identical with that found by Schützenberger in the case of animal compounds. It is clear, however, that the constitution of vegetable proteïds is different from that of animal proteïds. C. H. B.

Albumose. By H. SCHRÖTTER (*Monatsh.*, **14**, 612—623).—The author has prepared from Witte's commercial peptone an albumose, which is soluble in and crystallises from alcohol, is practically ash-less, and furnishes a hydrochloride of constant composition. The method employed is as follows :—The peptone is boiled with absolute methylic alcohol in a reflux apparatus, by which soluble impurities are removed. The residue is dissolved in water containing sulphuric acid, and is treated with zinc dust and sulphuric acid, the latter being added a little at a time. After remaining several days, and being warmed for four hours in a water bath, the solution is filtered, the sulphuric acid removed by excess of baryta, the clear solution saturated with carbonic anhydride, concentrated, again filtered, and eventually evaporated to dryness in a vacuum over sulphuric acid. The residue is exhausted with hot methylic alcohol, the extract concentrated, and the albumose precipitated with absolute ether. In order to obtain an ashless preparation, the albumose is subjected to treatment by Paal's process (compare Abstr., 1892, 895—897). The albumose dissolves readily in water and methylic alcohol; is sparingly soluble in cold alcohol; gives the biuret reaction characteristic of albumoses and peptones; is precipitated by tannin, mercuric chloride, ammonium sulphate, and sodium chloride; and contains, after allowing for 0·22—0·5 per cent. of ash, C 50·5—51·3, H 6·4—7·0, N 16·5—17·1, S 1·1 per cent. The *hydrochloride* contains C 47·2—48·5, H 6·5—7·3, N 14·6—14·7, S 0·9—1·1, HCl 10·5—11·0 per cent. The molecular weight of the albumose, as determined by

Raoult's method, in aqueous solution, was found to be between 587 and 714, whereas, if it be supposed that the molecule contains at least 1 atom of sulphur, the molecular weight, as deduced from analysis above, cannot be less than 2,000. In behaviour and composition the substance closely resembles the protalbumose described in *Beilstein's Handbuch*, **3**, 1304. On benzoylation, the albumose gives two products, of which one (C 60·8, H 5·8—6·0, N 12·6—12·8, S 0·9 per cent.) is crystalline, insoluble in alcohol, and yields on hydrolysis 19·7 per cent. of benzoic acid ; and the other (C 59·3—59·9, H 6·1—6·4, N 12·3—11·9 per cent.) is soluble in cold alcohol, contains apparently no sulphur, and yields on hydrolysis 17·5—18·6 per cent. of benzoic acid.   G. T. M.

Casein and the Organic Phosphorus of Casein. By A. BÉCHAMP (*Compt. rend.*, **117**, 1085—1088).—In order to detect and estimate phosphorus (and sulphur) in casein, a known weight of the dry compound is mixed with a standard solution of bismuth nitrate, evaporated to dryness, dried at 110°, and afterwards heated to dull redness. The difference between the total weight of the residue and the weight of the bismuth oxide gives the weight of the sulphuric and phosphoric acids.

Carefully purified casein of different preparations contains from 0·74 to 0·76 per cent. of phosphorus and 0·04 to 0·046 per cent. of sulphur. The insoluble product formed by the action of heat on casein contains 0·44 to 0·46 per cent. of phosphorus, and it is clear that phosphorus is an essential constituent of casein, and is present in organic combination.

Since casein contains both sulphur and phosphorus, it presents the first example of an immediate principle containing six elements.
                                                              C. H. B.

Synthesis of Hæmoglobins. By H. BERTIN-SANS and J. MOITESSIER (*Bull. Soc. Chim.*, [3], **9**, 721).—Hæmoglobins have been formed by combining bæmatins and proteïd substances obtained from the blood of sheep and fowls, both when the two constituents have been obtained from the blood of one animal species and when each constituent has had its origin in a different one of the three sources—cattle, sheep, and fowls.   W. T.

Displacement of the Carbonic Oxide in Carboxyhæmoglobin by Oxygen. By H. BERTIN-SANS and J. MOITESSIER (*Bull. Soc. Chim.*, [3], **9**, 722).—The displacement of carbonic oxide from carboxyhæmoglobin by aëration may be rapidly shown by a comparison of the spectra of two portions of blood saturated with carbonic oxide, after passing a rapid current of air through one and subsequently treating both with a solution of soda containing a little ammonium sulphide. The aërated sample shows the spectrum of hæmochromogen together with the much weakened spectrum of carboxyhæmoglobin; the other only shows the hæmochromogen spectrum after about an hour.
                                                              W. T.

Organic Chemistry.

Action of Sulphuric acid on Wood Charcoal. By A. VER-
NEUIL (*Compt. rend.*, **118**, 195—198).—When wood charcoal is heated
with concentrated sulphuric acid, the residue in the flask contains,
together with other acids which are under investigation, mellitic acid
and benzenepentacarboxylic acid identical with that obtained by Friedel
by the oxidation of pentamethylbenzene; 1400 grams of ordinary
sulphuric acid was heated with 100 grams of carbon, the process
being continued until only from 90 to 100 grams of residue remained
in the flask. The temperature of the reaction was about 280°, but
rose towards the end to about 300°, a rapid evolution of gas being
maintained in order to ensure that the water formed was expelled with
the carbonic and sulphurous anhydrides.

When the residue is treated with water, a dark brown solution is
formed, and a black, insoluble coagulum remains, showing no trace of
the original structure of the charcoal. It is soluble in alkalis and in
concentrated sulphuric acid, and is under investigation. The strongly
acid solution is mixed with just sufficient barium chloride to precipi-
tate the sulphuric acid, filtered, and evaporated to dryness, when a
brown, amorphous, strongly acid residue is left, equal in weight to
about 20 per cent. of the original carbon. When this residue is dis-
solved in water, saturated with ammonia, filtered and concentrated,
ammonium mellitate separates in quantity equal to about 4 per cent.
of the original carbon.

The mother liquor is evaporated with a slight excess of barium
hydroxide, and the barium salts are dissolved in hydrochloric acid,
and fractionally precipitated with barium hydroxide solution. The
first fraction carries down most of the colouring matter, whilst the next
fraction is crystalline, and consists of barium benzenepentacarb-
oxylate, which can be recrystallised from hydrochloric acid in the
form of an acid salt. C. H. B.

Substitution in the Aliphatic Series. By A. HERZFELDER
(*Ber.*, **27**, 489—490).—The author has made the conclusions given
in this vol. (i, 1) yet more sure, by affording additional confirma-
tion of the facts from which they are drawn. He proves that the
hexabromhexane, heptabromheptane, and octobromoctane are really
derivatives of the hexane, heptane, and octane, from which they
are respectively obtained on treatment with bromine and a little iron
wire, for he shows that these hydrocarbons are regenerated from
them when they are reduced with sodium in alcoholic solution.
C. F. B.

Tetramethylethylene Nitrosochloride. By J. THIELE (*Ber.*, **27**,
454—456).—The author gives directions for preparing pinacone by a
modification of Friedel's method. When pinacone hydrate is melted
in a beaker, and mixed with hydrobromic acid, saturated at 0° (5 parts),
crystals of tetramethylethylene bromide are deposited after 48 hours;

these are converted into tetramethylethylene (b. p. 73°), when treated with glacial acetic acid and zinc dust.

The *nitrosochloride*, $CMe_2Cl\cdot CMe_2\cdot NO$, prepared by the action of nitrosyl chloride, or better that of sodium nitrite and hydrochloric acid, on tetramethylethylene, is a blue powder, having a camphor-like penetrating odour; it melts at 121° with slight evolution of gas, volatilises in part undecomposed when boiled with water, and is only very slowly hydrolysed by alcoholic alkali in the cold. It does not give Liebermann's reaction, liberates iodine from potassium iodide in the cold, and yields silver chloride when treated with alcoholic silver nitrate.   A. R. L.

Gelatinous Silver Cyanide. By L. K. FRANKEL (*Chem. Centr.*, 1893, ii, 965; from *Proc. Chem. Sect. Frank. Inst.*, 1893, August).—With the intention of reducing the salt, some silver chloride was fused with potassium cyanide, the melt boiled with water, and the whole allowed to remain over night.   In the morning, the beaker was found to be filled with a transparent, gelatinous precipitate, similar to, but denser than, aluminium hydroxide.   On filtering and drying, the precipitate shrank together considerably.   It was soluble in ammonia, and was reprecipitated from this solution by nitric acid.   When heated, it did not fuse, but decomposed, metallic silver being left.   It gave the cyanogen reactions, but contained 5 per cent. less silver than pure argentic cyanide does.   The author believes the substance to have been a gelatinous form of silver cyanide, but has not succeeded in reproducing it.   L. T. T.

Preparation of Ferricyanides. By G. KASSNER (*Chem. Zeit.*, **17**, 1712—1713).—The author has previously described a method for the technical preparation of potassium ferricyanide by the action of carbonic anhydride on a mixture of potassium ferrocyanide and calcium plumbate (Abstr., 1890, 352).   The separation of potassium carbonate from potassium ferricyanide is attended with some difficulty; he suggests, therefore, the addition to the mixed potassium salts, after the oxidation, of sufficient calcium ferricyanide to decompose the whole of the potassium carbonate; if the liquids are heated, the precipitated calcium carbonate rapidly subsides.   Calcium ferricyanide is readily prepared from calcium ferrocyanide by the action of calcium plumbate and carbonic anhydride under pressure at the ordinary temperature; the resulting solution can be used directly.   For the preparation of the solid salt, it must be evaporated under reduced pressure, otherwise the calcium ferricyanide will be partially decomposed, as it is less stable than potassium ferricyanide.   J. B. T.

Configuration of Rhamnose and Galactose. By E. FISCHER and R. S. MORRELL (*Ber.*, **27**, 382—394).—The configuration of the sugars derived from mannitol has, for the most part, been cleared up during the past few years, but very little is known with regard to the configuration of those derived from dulcitol.   Mucic acid is known to contain an optically inactive system, but both the following formulæ fulfil this condition.

$$\begin{array}{cccc} H & OH & OH & H \\ | & | & | & | \\ COOH\cdot C & -C & -C & -C\cdot COOH \\ | & | & | & | \\ OH & H & H & OH \end{array} \qquad \begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ COOH\cdot C & -C & -C & -C\cdot COOH. \\ | & | & | & | \\ OH & OH & OH & OH \end{array}$$
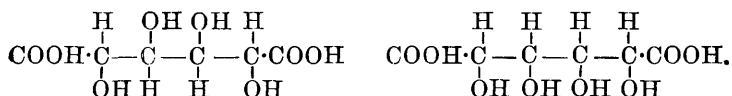
The investigation of rhamnose has unexpectedly led to the solution of the problem, inasmuch as this sugar, which belongs to the mannitol group, has been converted into mucic and talomucic acids, which are derived from dulcitol.

By the oxidation of rhamnose with nitric acid, Will and Peters (Abstr., 1889, 952) obtained the same trihydroxyglutaric acid that is formed from arabinose, the configuration of which is known. By the action of hydrogen cyanide on rhamnose, and subsequent hydrolysis, it is converted into rhamnohexonic acid, which must have the structure—

$$CH_3\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot \overset{*}{C}H(OH)\cdot COOH.$$

On oxidation, it yields large quantities of mucic acid, and, when heated with pyridine, rhamnohexonic acid is converted into a stereo-isomeric compound, which must, according to previous experience, differ from the first acid simply in the arrangement of the atoms around the carbon atom denoted by an asterisk in the above formula. The new acid, on oxidation, yields the optical isomeride of talomucic acid, which is itself obtained by the oxidation of d-galactose, and must, therefore, be termed d-talomucic acid, the new compound being the l-derivative.

The above changes are represented by the following scheme.

$$\text{Rhamnose} \longrightarrow \alpha\text{-Rhamnohexonic acid} \longrightarrow \beta\text{-Rhamnohexonic acid}$$
$$\downarrow \qquad\qquad\qquad \downarrow \qquad\qquad\qquad \downarrow$$

l-Trihydroxyglutaric acid.   Mucic acid. l-Talomucic acid.
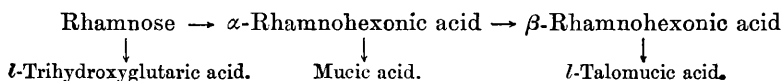
The configuration of all these compounds may be derived from the known configuration of l-trihydroxyglutaric acid in the following manner.

$$\begin{array}{ccc} OH & H & H \\ | & | & | \\ COOH\cdot C & -C & -C\cdot COOH \\ | & | & | \\ H & OH & OH \end{array} \qquad \begin{array}{ccc} OH & H & H \\ | & | & | \\ OH\cdot CHMe\cdot C & -C & -C\cdot CHO \\ \overset{?}{} & | & | \\ & H & OH & OH \end{array}$$

l-Trihydroxyglutaric acid.   Rhamnose.

$$\begin{array}{cccc} OH & H & H & OH \\ | & | & | & | \\ OH\cdot CHMe\cdot C & -C & -C & -C\cdot COOH \\ \overset{?}{} & | & | & | \\ & H & OH & OH & H \end{array}$$

α-Rhamnohexonic acid.

$$\begin{array}{cccc} OH & H & H & H \\ | & | & | & | \\ OH\cdot CHMe\cdot C & -C & -C & -C\cdot COOH \\ \overset{?}{} & | & | & | \\ & H & OH & OH & OH \end{array}$$

β-Rhamnohexonic acid.

r 2

$$\begin{array}{c} \text{OH H} \quad \text{H} \quad \text{OH} \\ | \quad | \quad | \quad | \\ \text{COOH·C —C —C —C·COOH} \\ | \quad | \quad | \quad | \\ \text{H} \quad \text{OH OH H} \end{array}$$
Mucic acid.

$$\begin{array}{c} \text{OH H} \quad \text{H} \quad \text{OH} \\ | \quad | \quad | \quad | \\ \text{OH·CH}_2\text{·C —C —C —C·CH}_2\text{·OH} \\ | \quad | \quad | \quad | \\ \text{H} \quad \text{OH OH H} \end{array}$$
Dulcitol.

$$\begin{array}{c} \text{OH H} \quad \text{H} \quad \text{H} \\ | \quad | \quad | \quad | \\ \text{COOH·C —C —C —C·COOH} \\ | \quad | \quad | \quad | \\ \text{H} \quad \text{OH OH OH} \end{array}$$
l-Talomucic acid.

$$\begin{array}{c} \text{H} \quad \text{OH OH OH} \\ | \quad | \quad | \quad | \\ \text{COOH·C —C —C —C.COOH} \\ | \quad | \quad | \quad | \\ \text{OH H} \quad \text{H} \quad \text{H} \end{array}$$
d-Talomucic acid.

$$\begin{array}{c} \text{H} \quad \text{OH OH OH} \\ | \quad | \quad | \quad | \\ \text{OH·CH}_2\text{·C —C —C —C·CHO} \\ | \quad | \quad | \quad | \\ \text{OH H} \quad \text{H} \quad \text{H} \end{array}$$
d-Talose.

$$\begin{array}{c} \text{H} \quad \text{OH OH H} \\ | \quad | \quad | \quad | \\ \text{OH·CH}_2\text{·C —C —C —C·CHO} \\ | \quad | \quad | \quad | \\ \text{OH H} \quad \text{H} \quad \text{OH} \end{array}$$
d-Galactose.

In the case of rhamnose and the rhamnohexonic acids, the configuration of the hydrogen and hydroxyl in combination with the carbon atom marked ? is still doubtful, and it is therefore uncertain whether they are derived from *l*-mannose or *l*-gulose.

The preparation of α-rhamnohexonic acid has already been described (Abstr., 1888, 806, 933, 1049). Its *phenylhydrazide* dissolves in 72 parts of water at 17°, and the *cadmium* salt, $(C_7H_{13}O_7)_2Cd$, crystallises in colourless, lustrous plates, and dissolves in 271 parts of water at 14°, and in about 20 parts at the boiling point. The *brucine* salt forms nodular aggregates of crystals, and melts at 120—123°. When treated with nitric acid of sp. gr. 1·2 at 40—45°, the chief product is mucic acid.

When heated with pyridine and water at 150—155°, α-rhamnohexonic lactone is converted partially into the optically isomeric β-*rhamnohexonic lactone*. In order to separate the two compounds, they are converted first into the barium salts and subsequently into the cadmium salts, the latter salt of the β-acid being readily soluble in water, whereas that of the α-acid is very slightly soluble. The solution of the β-cadmium salt is precipitated by hydrogen sulphide, and the solution of the free acid converted into the *brucine* salt, which forms spherical, crystalline aggregates, and melts at 114—118°. The free acid is obtained from the latter by boiling with baryta water, and decomposing the barium salt with sulphuric acid; on evaporation, the filtered solution yields a syrup, consisting chiefly of the lactone, which solidifies after a time, and crystallises from acetone in crusts of colourless, lustrous plates. It melts and decomposes at 134—138°; it is dextrorotatory, $[\alpha]_D$ being +43·34°, and remaining constant. The *phenylhydrazide* forms slender, lustrous plates, sinters at 160°, and melts at 170° with slight evolution of gas.

If the β-lactone is heated with pyridine, it is partly reconverted into the α-derivative; on reduction, it yields a sugar, which was not obtained in sufficient quantity for isolation, but which is converted by phenylhydrazine into the same rhamnohexosazone as α-rhamnohexose, thus proving that these two acids differ only in the arrangement of the atoms combined with the carbon atom next to the carboxyl group.

With nitric acid, β-rhamnohexonic lactone yields l-talomucic acid. To isolate this acid, it was converted into the *calcium* salt, which, after purification, has the composition $C_6H_8O_8Ca$. The free acid has the same melting point, crystalline form, and solubility as the d-talomucic acid, but is lævorotatory, $[\alpha]_D = -33·9°$. The *phenylhydrazide* crystallises in lustrous, pale yellow plates, and very closely resembles the d-derivative; it melts at 185° with decomposition, and, unlike mucic acid phenylhydrazide, dissolves readily in boiling water. l-Talomucic acid may be converted into mucic acid in the manner already described for the d-compound (Abstr., 1892, 299).

The configuration of d-galactose deduced from the foregoing experiments receives further confirmation from the fact that this sugar, on treatment with hydrogen cyanide and subsequent hydrolysis, yields, in addition to the carboxylic acid described by Kiliani, a stereoisomeric compound, which, like the latter, is optically active. This would be impossible if d-galactose had the formula

$$OH·CH_2·\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}·CHO$$
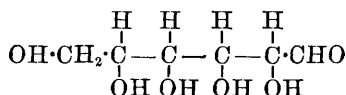
or its image, as one of the two pentahydroxypimelic acids must then have the configuration

$$COOH·\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}·COOH,$$
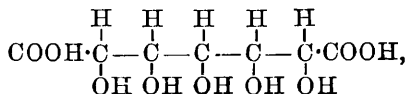
and would be optically inactive. H. G. C.

Compounds of the Sugars with Iron. By F. Evers (*Ber.*, **27**, 474—475).—*Iron sucrate*, containing about 48·5 per cent. of iron, is obtained as a crystalline, reddish-brown powder by pouring a solution of cane sugar and ferric chloride into a slight excess of aqueous sodium hydroxide; it dissolves to the extent of about 95 per cent. in cane-sugar solution, leaving a residue of ferric hydroxide.

Iron maltosate was prepared in the same way; it is a brown, amorphous substance, and is not mixed with free ferric hydroxide, for it dissolves entirely in maltose solution. It contains about 32 per cent. of iron, corresponding with the formula $2Fe_2O_3,C_{12}H_{22}O_{11} + 2H_2O$. C. F. B.

Crystalline Amido-derivatives of the Carbohydrates. By C. A. LOBRY DE BRUYN and A. P. N. FRANCHIMONT (*Rec. Trav. Chim.*, **12**, 286—289).—Ledderhose obtained so-called glucosamine hydrochloride by boiling chitin with hydrochloric acid; this base has also been studied by Tiemann (Abstr., 1884, 724; 1886, 329). Furthermore, Fischer obtained isoglucosamine by the reduction of ordinary glucosazone (Abstr., 1886, 933; 1888, 39). The direct transformation of the carbohydrates into amido-derivatives has not heretofore been observed.

In studying the two isomeric pentacetyl derivatives of glucose, the

authors observed that crystalline needles of glucosamine are slowly formed when the acetyl compounds are treated with alcoholic ammonia.

Further experiment showed that glucose itself is incapable of dissolving in ethyl alcoholic ammonia, but it dissolves freely in methyl alcoholic ammonia; after some weeks, the rotatory power of the solution gradually becomes less, and crystalline aggregates of the glucosamine last mentioned are deposited. This compound is not identical with that obtained from chitin.

Milk sugar and galactose are also insoluble in ethyl alcoholic ammonia, but dissolve in methyl alcoholic ammonia, forming crystalline osamines. The lactosamine seems to be an aldehyde-ammonia.

Fructose (levulose) dissolves in both ethyl alcoholic and methyl alcoholic ammonia, giving rise to a crystalline and an amorphous compound, which are probably isomeric, containing the same percentage of nitrogen as glucosamine.

The stability of these bases is very different: thus, glucosamine and lactosamine lose nitrogen as ammonia when boiled with N/10 sulphuric acid, and may be analysed by titration, whereas fructosamine is not decomposed under these circumstances.

It may be mentioned that this paper is only a preliminary communication on the subject, and no analytical data are given.

A. R. L.

Carbohydrates of Yeast. By E. SALKOWSKI (*Ber.*, **27**, 497—502). —A gum was obtained from German yeast, as free as possible from starch, by heating 500 grams of the yeast with 5 litres of 3 per cent potash, boiling for half an hour, siphoning off the liquid after a time, and heating it with 750 c.c. of Fehling's solution on the water bath. A copper compound of the gum was precipitated in bluish-white flakes; it was dissolved in water with the addition of a little hydrochloric acid, and the gum precipitated by adding alcohol; it was further purified by dissolving it in water and reprecipitating with alcohol, finally washing with alcohol and with ether. Thus prepared, it forms a fine, white powder, having the composition $C_{12}H_{22}O_{11}$, and specific rotation $[\alpha]_D = +90.1°$. It greatly resembles gum arabic, but, unlike the latter, it gives, in 1 per cent. aqueous solution, an immediate precipitate with Fehling's solution, but no turbidity when an equal volume of 1.12 per cent. hydrochloric acid and then 5 per cent. phosphotungstic acid are added. Acids convert the gum into a sugar; the latter is feebly dextrorotatory, reduces Fehling's solution, and is capable of undergoing fermentation. The gum is contained in the yeast to the extent of 2 per cent., that is, 7 per cent. of the dried material. No pentoses are present in the yeast. C. F. B.

Thermal Constants of Some Polyatomic Bases. By A. COLSON and G. DARZENS (*Compt. rend.*, **118**, 250—253).—*Ethylenediamine:* Specific heat. 0.84 between 12° and 45°; heat of dissolution at 15° = +7.6 Cal. Heat of neutralisation by hydrochloric acid, first equivalent = +12.50 Cal.; second equivalent, + 11.02 Cal.; total = 23.52 Cal. Heat of dissolution of the normal salt = −7.55 Cal. at about 15°.

Litmus and methyl-orange indicate the formation of the normal

salt, but with phenolphthaleïn the colour change takes place at a point intermediate between the normal salt and the basic salt. The existence of two basicities of not quite equal value is made evident by the thermochemical results only.

Quinine:—Heat of dissolution of the normal sulphate at about $11° = -6\cdot7$ Cal.; heat of neutralisation of the base by sulphuric acid in molecular proportion, $+ 15\cdot5$ Cal.

Basic quinine sulphate is generally supposed to have the composition $Q_2,H_2SO_4 + 7H_2O$, but analysis of a well crystallised specimen indicated the presence of $8H_2O$. Quinine contains a feeble basic function analogous to that of quinoline and a strong basic function similar to that of the amines of the ethylic, allylic, or piperidic series.

C. H. B.

Fractional Fermentation. The Amyloïns (Maltodextrins). By G. H. MORRIS and J. G. WELLS (*Trans. Inst. Brew.*, **5**, 133—172). —Starch transformations and beer worts of known optical activity and cupric reducing power were fermented with yeast, fractions being removed at intervals and the amounts of alcohol estimated in them; the alterations in optical activity and cupric reducing power were also noted. Practically the whole of the malt extract sugars are fermented in the first 48 hours, and, after this, the three estimations give identical results as to the amount of fermented matter calculated as maltose. Subsequently, that is, during the secondary fermentation, when all the free maltose has been removed, the quantity of alcohol formed and the optical activity indicate a larger amount of maltose than does the cupric reducing power. The authors assume that the amount of copper oxide reduced by any amyloïn is proportional to the quantity of combined maltose which it contains, whilst the amount of alcohol produced corresponds with the free maltose resulting from the hydrolysis of the amyloïns by the yeast.

Interesting results were obtained with two varieties of pure yeast, namely, Saaz yeast and Frohberg yeast; the former ferments about one-seventh less matter than the latter. The relative attenuations are uninfluenced by the quantity of yeast employed, the temperature, and degree of aëration of the wort, and they remained constant for six months. The addition of diastase caused a further fermentation in both cases. When a beer fermented to its fullest extent with Saaz yeast is sown with Frohberg yeast, fermentation recommences, and continues to the point it would have attained had the latter yeast been employed from the commencement. When crystallised maltose is added to a beer fermented to its lowest point by Saaz yeast, fermentation again sets in and continues until all the maltose is fermented. It is further shown that whilst Saaz yeast is incapable of fermenting anything beyond free maltose (probably on account of the absence of diastatic power), Frohberg yeast readily ferments the amyloïns of the low type, to which class the authors believe Lintner's so-called isomaltose to belong. A. R. L.

Hydroxylamine and its Homologues. By C. KJELLIN (*Ber.*, **27**, 587—588).—The author refers to a recent paper by Brühl on this

subject (this vol., i, 9), and points out that the results published simultaneously in his own paper (*loc. cit.*) were obtained independently of Brühl. β-Ethylhydroxylamine is much more stable than Brühl states, and, when pure, may be kept for several days without undergoing decomposition.   J. B. T.

Condensation of Isovaleraldehyde with Acetone. By P. Barbier and L. Bouveault (*Compt. rend.*, **118**, 198—201).—A mixture of isovaleraldehyde 100 parts, acetone 100 parts, sodium hydroxide solution (1 : 10) 100 parts, water 600 parts, is allowed to remain at the ordinary temperature with frequent agitation for three days; the supernatant layer of liquid is then separated, dried by means of fused sodium acetate, and fractionated. The greater part passes over between 170° and 190°, and obstinately retains water, which is removed by boiling it for a short time with acetic anhydride and again fractionating.

The purified product is a colourless mobile liquid of agreeable odour resembling that of amylic acetate; it has the composition $C_8H_{14}O$, boils at 180° under a pressure of 750 mm., sp. gr. at 0° = 0·8580; refractive index at 17·8 for λ645 = 1·4425 and for λ4526 = 1·4581.

With a hydrogen alkali sulphite, after long contact, it yields a crystallised product; when treated in the cold with a mixture of sodium hydroxide, sodium hypobromite, and potassium iodide it yields iodoform. It is also decomposed by the hypobromite alone but does not seem to yield bromoform. With Crismer's reagent it yields a liquid oxime, boiling, with slight decomposition, at 225—230° under ordinary pressure; this oxime yields a sodium salt insoluble in concentrated sodium hydroxide solution, and an oily benzoyl-derivative. When heated with alcohol and sodium, it yields a very small quantity of methylhexylcarbinol, together with a large quantity of a liquid substance of high boiling point, which seems to be the corresponding pinacone.

When oxidised with chromic mixture, the compound $C_8H_{14}O$ yields nothing but isovaleric acid, and, therefore, it must be regarded as *isoamylideneacetone*, $CHMe_2\cdot CH_2\cdot CH\cdot CH\cdot COMe$. It differs in its properties from the compound obtained by Wallach by the action of heat on cinoleïc anhydride, and therefore the latter is not isoamylideneacetone as Tiemann and Semmler supposed, but must have a different constitution, as Wallach originally stated.   C. H. B.

Heat of Combustion of Fatty Acids. By F. Stohmann, C. Kleber, H. Langbein, and P. Offenhauer (*J. pr. Chem.*, [2], **49**, 99—129).—The authors have redetermined the thermal values for the fatty acids (Abstr., 1886, 296). They describe the new method, and give the following values for solid acids (see next page).

It will be noted that the only two isomeric acids in the list have practically the same heat of formation. Formic acid should possess greater energy than acetic acid, for the difference between their heats of combustion is smaller than it should be; the same has been

observed in the case of oxalic acid in comparison with malonic acid. In their other relationships these two acids stand apart from the rest of those in their series, indicating that they are more energetic compounds (compare Ostwald, *Lehrbuch*, [2], **2**, i, 650).

	Heat of combustion. Cal.	Difference. Cal.	Heat of formation. Cal.
Formic acid, CH_2O_2	59·0		104·0
Acetic acid, $C_2H_4O_2$	206·7	147·7	119·3
Propionic acid, $C_3H_6O_2$	364·0	157·3	125·0
Normal butyric acid, $C_4H_8O_2$	520·4	156·4	131·6
Normal valeric acid, $C_5H_{10}O_2$	677·2	156·8	137·8
Isobutylacetic acid, $C_6H_{12}O_2$	832·2⎫	⎧155·0⎫	⎧145·8
Diethylacetic acid, $C_6H_{12}O_2$	832·3⎭	⎩155·1⎭	⎩145·7
Ethylpropylacetic acid, $C_7H_{14}O_2$	988·8	156·5	152·2
Dipropylacetic acid, $C_8H_{16}O_2$	1145·0	156·2	159·0
Heptylacetic acid, $C_9H_{18}O_2$	1302 3	157·3	164·7
Normal capric acid, $C_{10}H_{20}O_2$	1458·3	156·0	171·7
Undecylic acid, $C_{11}H_{22}O_2$	1615·9	157·6	177·1
Lauric acid, $C_{12}H_{24}O_2$	1771·8	155·9	184·2
Myristic acid, $C_{14}H_{28}O_2$	2085·9	157·0 × 2	196·1
Palmitic acid, $C_{16}H_{32}O_2$	2398·4	156·2 × 2	209·6
Stearic acid, $C_{18}H_{36}O_2$	2711·8	156·7 × 2	222·2
Arachidic acid, $C_{20}H_{40}O_2$	3025·8	157·0 × 2	234·2
Behenic acid, $C_{22}H_{44}O_2$	3338·3	156·3 × 2	247·7

The following figures for bibasic acids are given :—

	Heat of combustion.	Heat of formation.
Malonic acid, $C_3H_4O_4$	207·3	212·7
Methylmalonic acid, $C_4H_6O_4$	362·5	220·5
Ethylmalonic acid, $C_5H_8O_4$	517·9	228·1
Dimethylmalonic acid, $C_5H_8O_4$	515·3	230·7
Methylethylmalonic acid, $C_6H_{10}O_4$	676·0	233·0
Isopropylmalonic acid, $C_6H_{10}O_4$	675·2	233·8
Propylmalonic acid, $C_6H_{12}O_4$	675·0	234·0
Diethylmalonic acid, $C_7H_{12}O_4$	832·9	239·1
Ethylpropylmalonic acid, $C_8H_{14}O_4$	989·9	245·0
Dipropylmalonic acid, $C_9H_{16}O_4$	1146·1	251·9
Heptylmalonic acid, $C_{10}H_{18}O_4$	1302·7	258·3
Octylmalonic acid, $C_{11}H_{20}O_4$	1458·5	265·5
Cetylmalonic acid, $C_{19}H_{36}O_4$	2707·7	320·3

The following conclusions concerning the formation of acids from the corresponding hydrocarbons, may be drawn :—(1) The reaction .—H+COOH is not represented by any constant thermal change. (2) The formation of solid monobasic saturated acids from the solid hydrocarbons is accompanied by a loss of energy represented by from 2·4 to 4·4 Cal. (3) In the transition of the monobasic saturated acids to the malonic acids, the thermal change is nearly nil. (4) In the

transition of acetic to malonic acid and of formic to oxalic acid, there is an increase of energy represented by 0·6 Cal. and 0·8 Cal. respectively. (5) In the transition of solid monobasic acids to normal bibasic acids (except oxalic and malonic acids) there is a regular loss of energy, amounting to 5·1—8·3 Cal. in the groups with an even number of carbon atoms and to 3·3—5·4 Cal. in those with an uneven number of carbon atoms. (6) In the succinic series the transition of solid monobasic acids is accompanied by a regular loss of energy represented by 2·7—7·2 Cal.

The heat of combustion of allylmalonic acid, $C_6H_8O_4$, is 638·1 Cal.; that of benzylmalonic acid, $C_{10}H_{10}O_4$, is 1085·9 Cal.; that of tricarballylic acid is 516·3 Cal.　　　　　　　　　　A. G. B.

Cryoscopic Behaviour of Acetates of Feeble Bases. By A. GHIRA (*Gazzetta*, **23**, ii, 598—601).—The acetates of triethylamine, diethylamine, piperidine, and coniine exercise abnormal depressions on the freezing point of benzene; their behaviour is thus analogous to that of the acetates previously examined by the author (Abstr., 1893, i, 667).　　　　　　　　　　　　　　　　　W. J. P.

Solubility of Silver, Calcium, and Barium Œnanthylate, and of Calcium and Barium Trimethylacetate. By H. LANDAU (*Monatsh.*, **14**, 707—718).—The solubilities were determined according to Raupenstrauch's method (*Monatsh.*, 1885, 563). Solubility curves are given in the original paper. The following equations were calculated from the results:—

Silver œnanthylate, $S = 0·063475 + 0·00188089t + 0·000001303t^2 + 0·00000006429t^3$.

Barium œnanthylate, from 1·6 to 30·7°, $S = 1·7602 + 0·00340552 (t—1·6) — 0·0000040143(t — 1·6)^2$; from 30·7 to 83·5°, $S = 1·6577 + 0·00609193(t—30·7) + 0·000168803(t — 30·7)^2$.

Calcium œnanthylate from 2 to 15·8°, $S = 0·88986 — 0·0033093(t—2) — 0·00031334(t — 2)^2$; from 15·8 to 41°, $S = 0·7849 — 0·00034732 (t — 15·8) + 0·000017719(t — 15·8)^2$; from 41 to 76°, $S = 0·7874 + 0·004943(t — 41) — 0·00006826(t — 41)^2$.

Barium trimethylacetate, $S = 34·2546 — 0·0356536(t — 2) — 0·00251518(t — 2)^2 + 0·000047568(t — 2)^3$.

Calcium trimethylacetate, from 1 to 37·3°, $S = 7·2424 — 0·0517276 (t — 1) + 0·00077773(t — 1)^2$; from 37·3 to 78·5°, $L = 6·3894 + 0·0177155(t — 37·3) + 0·00013074(t$ to $37·3)^2$.　　E. C. R.

Parasorbic Acid. By O. DOEBNER (*Ber.*, **27**, 344—351).—Parasorbic acid, $C_6H_8O_2$, was prepared by the author from the residue left after the extraction of malic acid from the juice of mountain ash berries. On distillation with steam and subsequent purification, it boiled at 221° under atmospheric pressure, and at 136° under 30 mm., a small quantity of resinous matter being always left behind. It did not solidify in a freezing mixture, and at 21° had the sp. gr. 1·0628. When pure it had no acid reaction, but became acid on standing. It

is dextrorotatory, having the specific rotation $[\alpha]_j = +40\cdot8°$, and its heat of of combustion is $758\cdot4$ Cal.

It combines with bromine, yielding an oil of the composition $C_6H_8O_2Br_2$. No tetrabromide could be obtained.

Its salts do not correspond with an acid $C_6H_8O_2$, but with an acid $C_6H_{10}O_3$, the barium salt, for instance, being $Ba(C_6H_9O_3)_2$. The ethylic salt could not be prepared, ethylic sorbate being obtained in its stead.

Parasorbic acid passes into the isomeric sorbic acid when heated for a short time with solid potash and a few drops of water, the yield being 70 per cent. Sorbic acid on the other hand cannot be transformed into parasorbic acid.

These reactions point to the conclusion that whereas sorbic acid is a doubly unsaturated acid, $CH_3\cdot CH\!:\!CH\cdot CH\!:\!CH\cdot COOH$, the isomeric parasorbic acid is the lactone of a singly unsaturated acid, its formula being in all probability, $CH_3\cdot CH_2\cdot CH{<}^{-\ CH}_{O\cdot CO}{>}CH.$ J. W.

Crystalline Constituent of the Fruit of Picramnia Camboita Engl. By B. Grützner (*Chem. Zeit.*, **17**, 1851—1852).—The author has previously described an acid from the fat of the fruit of *picramnia camboita Engl.*; further investigation has shown that the fat is a triglyceride of tariric acid, and is, therefore, identical with the fat obtained by Arnaud from the seeds of a shrub belonging to the genus *Picramnia* or *Tarari* (Abstr., 1892, 582). *Silver tarirate* crystallises in needles, darkens slowly on exposure to light, and commences to decompose at 160°. The *barium salt* is amorphous and anhydrous, and becomes yellow at 180°. The dibromoadditive compound melts at 32°. The tetrabromo-derivative, $C_{18}H_{32}Br_4O_2$, melts at 138° instead of 125° as stated by Arnaud (*loc. cit.*).   J. B. T.

Remarkable Intramolecular Change. By A. Hantzsch (*Ber.*, **27**, 355—356).—The author has repeatedly shown that the sole product in the direct bromination of ethylic acetoacetate is ethylic γ-bromacetoacetate (compare this vol., i, 171), whilst, on the other hand, the bromination of ethylic cupracetoacetate leads to the exclusive formation of ethylic α-bromacetoacetate. Experiments made with a sample of the α-derivative which had been prepared some months previously showed that it had undergone alteration, and further investigation proved that this compound, when allowed to remain at the ordinary temperature, is gradually converted into ethylic γ-bromacetoacetate. As to the manner in which the change takes place nothing definite is known, but it may possibly be due to the intermediate formation of a trimethylene derivative, which then again reunites with the liberated hydrogen bromide, forming the γ-derivative. A somewhat similar intramolecular change has been observed by Wolff (Abstr., 1891, 416) who obtained glyoxylpropionic acid, $CHO\cdot CO\cdot CH_2\cdot CH_2\cdot COOH$, by boiling dibromolevulinic acid, $CH_3\cdot CO\cdot CBr_2\cdot CH_2\cdot COOH$, with water.   H. G. C.

Electrolysis of Salts of Organic Acids. By W. v. MILLER and J. HOFER (*Ber.*, **27**, 461—470).—When a concentrated solution of sodium glycollate is electrolysed, no synthetic product is obtained, the acid undergoing oxidation to formaldehyde, carbonic anhydride, and carbonic oxide at the positive pole. Sodium α-hydroxybutyrate yields propaldehyde and a little formic acid as oxidation products, and the corresponding α-hydroxyisobutyrate yields acetone in addition. Potassium tartrate does not yield acetic acid and ethylene, as Bourgoin states, but formaldehyde and formic acid. Sodium β-hydroxybutyrate, when electrolysed, gives off unsaturated hydrocarbons at the positive pole. The salts of phenyl-β-lactic acid and mandelic acid yield benzaldehyde besides carbonic anhydride and carbonic oxide. The alkaline methoxyacetates give off the usual gases, the other oxidation products being formaldehyde, formic acid, methylal, and methylic alcohol.   J. W.

Formula of the so-called Oxybrassidic acid. By M. FILETI (*J. pr. Chem.*, [2], **49**, 200).—The author corrects Baruch's quotation (Abstr., 1893, i, 393) of his (the author's) statement that the formula in question is $C_{22}H_{42}O_3$, not $C_{22}H_{40}O_3$.   A. G. B.

Hydration of the Calcium Salts of Succinic and Methylethylacetic acids. By D. MILOJKOVIĆ (*Monatsh.*, **14**, 699—706).— Calcium succinate, when crystallised at 20—22°, contains $3H_2O$. At 80—85° it crystallises with $1H_2O$. When the salt with $3H_2O$ is shaken with water at 60° it is converted into the salt with $1H_2O$, and the salt with $1H_2O$, when shaken with water at 23°, is converted into the salt with $3H_2O$. These results explain the bend which occurs at about 30° in the curve of solubility of calcium succinate. Calcium methylethylacetate, when crystallised at 23—26°, contains $3H_2O$; crystallised at 85—90°, it contains $1H_2O$. The two salts are convertible one into the other, in the same way as the calcium succinates of different degrees of hydration. When the salt with $3H_2O$ is shaken with water at 0° it is converted into a salt with $5H_2O$. These different degrees of hydration are shown on the solubility curve of the salt.   E. C. R.

Action of Nitrous Acid on Ethylic Acetylglutarate. By G. BALDRACCO (*J. pr. Chem.*, [2], **49**, 196—199).—γ-*Isonitrosoacetobutyric acid*, $COMe \cdot C(NOH) \cdot CH_2 \cdot CH_2 \cdot COOH$, is prepared by hydrolysing ethylic acetylglutarate with an alkali, adding sodium nitrite and acidifying; the new compound is dissolved out by shaking with ether. It crystallises from chloroform in large, transparent, colourless prisms (with $CHCl_3$), melts at 97—97·5°, and dissolves freely in alcohol, ether, and warm water, moderately in benzene and chloroform, but not at all in carbon bisulphide or light petroleum. Its alkaline solutions show the yellow colour characteristic of the $-CO \cdot C\!:\!NOH$ group. The *barium* salt, with $3H_2O$, and the *hydrazone* (m. p. 168°) are described. With hydroxylamine, it yields γδ-*di-isonitrosocaproic acid*, $NOH\!:\!CMe \cdot C(NOH) \cdot CH_2 \cdot CH_2 \cdot COOH$, which

crystallises in prisms, melts at 180·5°, and dissolves in water, alcohol, and ether ; its solutions in alkalis are colourless. A. G. B.

Action of Ethylic Sodiomalonate on Cyanuric Chloride. By W. KOLB (*J. pr. Chem.*, [2], **49**, 90—99).—In attempting to obtain a trisubstitution product from cyanuric chloride by its action on ethylic sodiomalonate, the author isolated a *compound* which crystallises in needles, melts at 190° and has a molecular weight corresponding with the formula $C_{24}N_3H_{33}O_{12}$.

Ethylic dihydroxycyanuromalonate,

$$N\ll^{C(OH)\cdot N}_{C(OH):N}\gg C\cdot CH(COOEt)_2,$$
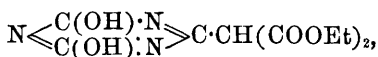
was prepared by mixing cyanuric chloride with ethylic sodiomalonate in molecular proportion. It crystallises in white, lustrous needles, melts at 181°, and dissolves in alcohol and ether, but not in carbon bisulphide. The *silver* derivatives, $C_{10}N_3H_{10}Ag_3O_6$ and $C_{10}N_3H_{12}AgO_6$, were obtained respectively by adding silver nitrate to an ammoniacal and to a neutral aqueous solution of the ethylic salt ; the latter, when heated with methylic iodide, yields a *monomethylic* derivative as a white crystalline mass of ill-defined melting point. Attempts to separate the acid by hydrolysing the ethylic salt with potash failed. When strong hydrochloric acid at 130° is used as the hydrolysing agent, *dihydroxycyanuracetic acid,* $N\ll^{C(OH)\cdot N}_{C(OH):N}\gg C\cdot CH_2\cdot COOH,$

is isolated ; this crystallises in needles, decomposes at 180° without melting, and dissolves in water and dilute alcohol. The *silver* derivative, $C_5N_3H_2Ag_3O_4$, was prepared ; when it is heated with methylic iodide in methyl alcohol, it is converted into *dihydroxycyanuromethane,* $C_3N_3(OH)_2Me$ (with 1 mol. H_2O), a crystalline mass, whose *silver* derivative, $C_4N_3H_3Ag_2O_2$, was prepared. A. G. B.

Rotatory Power of Tartrates. By R. PŘIBRAM (*Monatsh.*, **14**, 739—745).—The author finds the following numbers for the rotatory power of the salts of tartaric acid in aqueous solution at 20°, P being the percentage strength of the solution, in each case corresponding with 0·2 gram of tartaric acid in 100 c.c. of water.

	P.	$[\alpha]_D$.	$[M]_D$.
$Li_2C_4H_4O_6$	0·216	35·58	57·63
$(NH_4)_2C_4H_4O_6$	0·245	35·46	65·24
$Na_2C_4H_4O_6$	0·2589	31·11	60·35
$K_2C_4H_4O_6$	0·3015	25·62	57·90
$Rb_2C_4H_4O_6$	0·4247	18·97	60·32
$Cs_2C_4H_4O_6$	0·5522	13·78	57·04
$Tl_2C_4H_4O_6$	0·7417	8·56	47·50
$NaHC_4H_4O_6$	0·2293	27·11	46·62
$KHC_4H_4O_6$	0·2505	21·57	40·17
$RbHC_4H_4O_6$	0·3116	18·38	43·00
$CsHC_4H_4O_6$	0·3754	15·84	44·67
$TlHC_4H_4O_6$	0·4692	12·07	42·57

It thus appears that Oudemann's law is obeyed by all the alkali tartrates with the exception of normal thallium tartrate (compare this vol. ii, 78). J. W.

Oxidation of Saccharic and Mucic acids with Potassium Permanganate. By E. FISCHER and A. W. CROSSLEY (*Ber.*, 27, 394—398).—It has long been known that saccharic acid on further oxidation with nitric acid yields tartaric acid, and that mucic acid under similar conditions is partly converted into racemic acid, but the results hitherto obtained have not been sufficiently definite to allow of conclusions being drawn as to the configuration of the two acids. The authors find that if a dilute solution of alkaline potassium permanganate is employed in place of nitric acid, much more satisfactory results are obtained, saccharic acid being thus converted into dextro-tartaric acid and an excess of oxalic acid, and mucic acid into racemic acid and oxalic acid. This reaction confirms the configuration of mucic acid deduced in the previous paper (this vol., i, 218), for the oxidation of an acid of this configuration might take place in two different ways, yielding in one case dextro- and in the other lævo-tartaric acid ; and as the probability for both reactions is equal, the resulting compound is racemic acid.

With saccharic acid, the oxidation might also proceed in two different ways, leading to the formation of either dextro- or lævo-tartaric acid, but as a matter of fact only the dextro-acid is formed. Which of the two theoretically possible reactions actually occurs can only be decided when the exact relation of the configuration of dextrotartaric acid to glucose is known. The authors endeavoured to ascertain this by the oxidation of *d*-mannonic acid, which could only form one tartaric acid, but the yield obtained was so small that no definite conclusions could be drawn from it. H. G. C.

Conversion of Orthodiketochlorides into Chlorinated Keto-R-pentenes by Bleaching Powder. By T. ZINCKE (*Ber.*, 27, 562—564).—The orthodiketochlorides described in another paper (this vol., i, 234) are not converted by the usual reaction into chlorinated keto-R-pentenes of the $\gamma\gamma$-series, compounds of the $\beta\gamma$-series alone being formed. Compounds of both series are, however, formed at the same time, when the ketochlorides are dissolved in methylic alcohol and treated with an aqueous solution of bleaching powder. The three following $\gamma\gamma$-compounds have been thus prepared, $CO<\begin{smallmatrix}CCl_2 \cdot CCl\\CCl_2 \cdot CMe\end{smallmatrix}$,
$CO<\begin{smallmatrix}CClMe \cdot CCl\\CCl_2 - CCl\end{smallmatrix}$, $CO<\begin{smallmatrix}CCl_2 - CMe\\CClMe \cdot CCl\end{smallmatrix}$, whilst the $\beta\gamma$-compounds $CO<\begin{smallmatrix}CCl:CMe\\CCl_2 \cdot CCl_2\end{smallmatrix}$, $CO<\begin{smallmatrix}CMe:CCl\\CCl_2 \cdot CCl_2\end{smallmatrix}$, have been obtained by the usual method. The $\gamma\gamma$-ketones resemble the already known ketone, C_5Cl_6O, but do not react like it with ammonia. A. H.

Behaviour of Cinnamic Dichloride towards Micro-organisms. By A. STAVENHAGEN and H. FINKENBEINER (*Ber.*, 27, 456—457). —Cinnamic dichloride has been partially resolved into its optically

active components by Liebermann and Finkenbeiner (Abstr., 1893, i, 415). The authors have treated 5 grams of the dichloride for four weeks with *Aspergillus fumigatus*, and isolated 1·5 grams of an acid rotating $[\alpha]_D = + 1$. From 6 grams of dichloride treated with yeast for three weeks, 2·2 grams of an acid was obtained, giving $[\alpha]_D = + 2·8$. The organisms had multiplied during the above periods, despite the formation of hydrogen chloride and chlorocinnamene. Blank experiments (without the organisms) showed that whilst a small quantity of chlorocinnamene was formed, the acid remained inactive.

A. R. L.

Ketochlorides Derived from Phenol. By T. ZINCKE and C. SCHAUM (*Ber.*, **27**, 537—559).—Tetrachloroketodihydrobenzene, $C_6Cl_4H_2O$, has been previously prepared by Benedikt (*Monatsh.*, **4**, 233) from symmetrical trichlorophenol by the action of chlorine, but a better yield is obtained by the use of bleaching powder. The compound crystallises in almost colourless monosymmetric prisms, with a vitreous lustre, and melts at 122° (119° Benedikt). It is readily reconverted into trichlorophenol by the action of alkalis or acids. The position of the substituent groups is one of the following ($O : Cl_2 : Cl : Cl = 1 : 2 : 4 : 6$ or $1 : 4 : 2 : 6$).

Hexachloroketodihydrobenzene, C_6Cl_6O, may be obtained from pentachloraniline by the action of chlorine (Langer, *Annalen*, **215**, 122) or from di- and tri-chloraniline [$1 : 3 : 5$ and $1 : 3 : 4 : 5$. $NH_2 = 1$], but it is best prepared by heating α-heptachloroketotetrahydrobenzene (m. p. 98°) at 200—210°, the elements of hydrogen chloride being eliminated and the hexachloro-compound formed. The corresponding β-heptachloro-compound (m. p. 80°) yields the hexachloroketone when heated with an excess of potassium acetate and glacial acetic acid. Hexachloroketodihydrobenzene forms either tabular or needle-shaped crystals of the quadratic system. It melts at 106° and decomposes at 260° with formation of a substance of the formula $C_{12}Cl_8O_2$. It is converted into pentachlorophenol by reduction or by heating with 90 per cent. acetic acid; in acetic acid or chloroform solution, it is not altered by chlorine. It reacts with sodium methoxide, yielding the same substance as the heptachloroketones, from the nature of which its constitution has been deduced.

Heptachloroketotetrahydrobenzene, C_6Cl_7HO.—Two compounds of this formula are produced by the action of chlorine on metachloraniline dissolved in acetic acid, the α-isomeride being formed in larger quantity. The substance melting at 78·5—80°, described by Beilstein (*Ber.*, **11**, 2182) as formed by the chlorination of meta-chloracetanilide, is probably a mixture of these. The *α-compound* crystallises in large, lustrous, monosymmetric prisms, which lose their lustre and transparency after a time. It is readily soluble in ether, chloroform, &c., less readily in light petroleum, and has a characteristic camphor-like odour. It melts at 98°, and decomposes at 170°, the hexachloroketone being formed. It is very readily reduced to tetrachlorophenol (Zincke and Wallbaum, Abstr., 1891, 708) by stannous chloride, sodium sulphite, or potassium iodide, and is converted into pentachlorophenol when boiled with potassium acetate and acetic acid or if heated with alcohol at 250°.

The *β-compound* forms lustrous, rhombic crystals, and behaves towards solvents in a similar manner to the α-compound. It melts at 80°, and when heated to 220° loses the elements of hydrogen chloride and chlorine, forming the compound $C_{12}Cl_8O_2$, which crystallises in soft, lustrous, white needles, does not melt below 280°, and is remarkably stable towards reagents. The β-heptachloro- ketone is reduced by stannous chloride to tetrachlorophenol, and by sodium sulphite and potassium iodide to pentachlorophenol, and when heated with potassium acetate, yields the hexachloroketo-compound, identical with that obtained by simply heating the isomeric α-heptachloroketone.

Action of Sodium Methoxide on Hexa- and Hepta-chloroketotetrahydrobenzene.—When one of these ketochlorides is dissolved in methylic alcohol and treated with sodium methoxide, the liquid being filtered from the common salt which separates, and then acidified, a substance of the formula $C_6Cl_3(OMe)_4·OH$ is precipitated; this is sparingly soluble in ether, or light petroleum, but more readily in acetic acid, acetone, or methylic alcohol, from the last of which it separates in transparent, well-developed, tabular crystals, melting at 142—143°. It has a distinctly acid character, and forms a yellow, crystalline *barium salt.* When heated with aqueous soda or baryta water, it is converted into the compound $C_6Cl_3(OMe)_2(OH)O$, which is soluble in alkalis, whilst acids remove all the methoxy-groups, forming trichlorohydroxyquinone, $C_6Cl_3(OH)O_2$. When heated alone or in solution, the methylate loses a molecule of methylic alcohol, and forms the neutral compound $C_6Cl_3(OMe)_3O$, which is readily soluble in alcohol, &c., sparingly in light petroleum, crystallises in thick, transparent, yellow tablets, and melts at 78°. When a few drops of an aqueous alkali are added to its solution in methylic alcohol, it is reconverted into the tetramethoxy-derivative. It combines in the same manner with ethylic alcohol to form an *ethylate,* which forms small, white needles, melting at 140° with decomposition.

The compound $C_6Cl_3(OMe)_3O$, as well as its methylate, is converted by reduction into *trichlorodimethoxyphenol,*
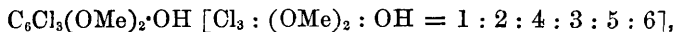
$$C_6Cl_3(OMe)_2·OH \ [Cl_3 : (OMe)_2 : OH = 1 : 2 : 4 : 3 : 5 : 6],$$

which is readily soluble in alcohol, and crystallises in long, colourless needles melting at 110°. It dissolves without change in alkalis and alkali carbonates and yields an *acetate* which forms thick tablets and melts at 65°. Trichlorodimethoxyphenol is converted, by treatment with nitric acid, into *trichloroparamethoxyorthoquinone,* $C_6Cl_3(OMe)O_2$, which crystallises in deep red plates melting at 93—94°. It is reduced by aqueous sulphurous acid to *trichloroparamethoxycatechol,* $C_6Cl_3(OMe)(OH)_2$, which forms thick, pointed crystals melting at 118°. It is sparingly soluble in water, readily in alcohol and in aqueous alkalis, and is oxidised by nitric acid to the quinone. Its *acetate* crystallises in aggregates of short, thick needles melting at 103.

When the trichloromethoxyquinone is dissolved in acetic acid and concentrated hydrochloric acid is added, the red colour of the solution at first considerably deepens, and the liquid then probably contains

trichloroparahydroxyorthoquinone [O : O : OH = 1 : 2 : 4] ; it soon becomes lighter in colour, however, and deposits the isomeric *trichlororthohydroxyparaquinone* [O : OH : O = 1 : 2 : 4], formed by intramolecular change ; the latter is best prepared by boiling an acetic acid solution of the methylate with hydrochloric acid. When the substance is slowly crystallised from ether, orange-red prisms are obtained, but, on heating, these are converted into a yellow powder, which melts at 194° ; this yellow powder is reconverted into the orange-red crystals by slow crystallisation from ether containing a little acetic acid. The quinone forms a deep-violet coloured solution in water, which is decolorised by mineral acids; its solution in aqueous soda is colourless, but becomes violet on dilution. When heated with an alkali, it is converted into chloranilic acid. On reduction, it is converted into *trichloroparahydroxyquinol*, $C_6Cl_3(OH)_3$, which melts at 160° and separates from benzene or acetic acid in crystals containing benzene or acetic acid of crystallisation. Its solution in water is colourless, but becomes violet when heated, whilst in alkalis it forms deep-green solutions, which become brown on standing, the quinone being formed. The *acetate* forms fine, white needles melting at 171°.

When the tetramethoxide, $C_6Cl_3(OMe)_4HO$, or the compound $C_6Cl_3(OMe)_3O$, is heated with dilute aqueous soda, it is converted into a substance of the formula $C_6Cl_3(OMe)_2(OH)O$, which forms thick, almost colourless needles melting at 159—160°. The *barium salt*, with $2H_2O$, crystallises in small, golden-yellow, lustrous tablets. The *acetate* forms colourless prisms melting at 91°. This substance is readily converted into trichlorohydroxyparaquinone by boiling with water or acids, but not in presence of alkalis.

Trichlororthomethoxyquinol, $OMe \cdot C_6Cl_3(OH)_2$, isomeric with the trichloromethoxycatechol, described above, is obtained from the foregoing compound by reduction with zinc dust in alkaline solution. It forms compact, colourless crystals melting at 116°. The *acetate* is readily formed, but has not been obtained in the crystalline state.

It follows from the nature of the reaction of the hexa- and heptachloroketones with sodium methoxide, that these compounds must be represented by the following formulæ.

$$CO<^{CCl_2 \cdot CCl}_{CCl : CCl}>CCl$$

Hexachloroketone.

$$CO<^{CCl_2 \cdot CHCl}_{CCl : CCl-}>CCl_2 \qquad CO<^{CCl_2 \cdot CCl}_{CCl_2 \cdot CHCl}>CCl$$

Heptachloroketones.
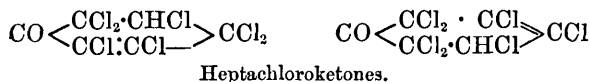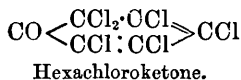
Which of the two formulæ must be ascribed to the α- and which to the β-heptachloroketone has not yet been decided.

Octochloroketotetrahydrobenzene, which has been prepared by Benedikt (*Monatsh.*, **4**, 607), from pentachlorophenol and by Zincke and Wallbaum from perchlorometahydroxybenzoic acid, cannot be prepared from the hexachloroketone and does not react with sodium methoxide in the cold. It has probably one of the following formulæ :

$$ \{CO{<}^{CCl_2\cdot CCl}_{CCl_2\cdot CCl_2}{>}CCl, \qquad CO{<}^{CCl_2\cdot CCl_2}_{CCl{=\!=}CCl}{>}CCl_2. $$

1 : 3 : 4 : 5-*Trichloraniline*, employed in the preparation of the hexachloroketone, is obtained from dichloropaianitraniline by means of the diazo-reaction and subsequent reduction. It forms long, brittle needles and melts at 100°.   A. H.

Action of Chlorine on Ortho- and Para-Diamines. By T. ZINCKE (*Ber.*, **27**, 560—562).

—The chlorinated orthodiketones and orthoquinones have hitherto been prepared either directly from the quinones, or their reduction products, or by the action of chlorine on the hydrochlorides of the amidophenols. In addition to these methods, they may be readily obtained by the action of chlorine on the hydrochlorides of the orthodiamines dissolved in acetic acid. In this way, diketochlorides of toluene, trichlorotoluene, and metaxylene have been prepared, $CMe{<}^{CCl_2\cdot CCl_2}_{CCl-CO}{>}CO$, $CMe{<}^{CCl\cdot CCl_2}_{CO-CO}{>}CCl_2$, $CClMe{<}^{CCl:C_2Me}_{CCl_2-CO}{>}CO$, and these have been converted, by reduction and subsequent oxidation, into numerous derivatives. Similar derivatives have also been obtained from orthodiamidopseudocumene. These diketochlorides resemble hexachlorodiketone, $C_6Cl_6O_2$, in their general properties, but do not react in the usual manner with alkalis. The paradiamines may also be employed in a similar manner.

A. H.

Derivatives of Chloracetocatechol and Chlorogallacetophenone. By S. K. DZERZGOVSKY (*J. Russ. Chem. Soc.*, **25**, 275—291).

—*Dimethylamidoacetocatechol*, $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NMe_2$, is prepared by the action of dimethylamine (2 mols.) on chloracetocatechol (1 mol.) in alcoholic solution. The base itself can only be obtained with great difficulty. The oxalate, however, crystallises well from alcohol and from water, in colourless prisms which melt at 235° with partial decomposition. The hydrochloride can be obtained from the oxalate by precipitation with calcium chloride, and crystallises from water in needles melting at 232°.

Dimethylamidoacetopyrogallol, $C_6H_2(OH)_3\cdot CO\cdot CH_2\cdot NMe_2$, can be prepared in like manner, chloracetopyrogallol being used instead of chloracetocatechol. The oxalate and tartrate crystallise in colourless prisms, melting at 190° and 205—206° respectively.

Anilidoacetocatechol, $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NHPh$, crystallises from alcohol in greenish-yellow prisms, melting at 149°. The corresponding orthotoluidide and paratoluidide melt at 157° and 103° respectively. Methylanilidoacetocatechol melts at 155°, and is sparingly soluble in boiling water.

Methylanilidoacetopyrogallol, $C_6H_2(OH)_3\cdot CO\cdot CH_2\cdot NMePh$, crystallises in yellow plates, melting at 168°.

Dimethylaniline acts on the chloro-derivatives of acetopyrogallol and acetocatechol with formation of the *chlorides*

$$ C_6H_2(OH)_3\cdot CO\cdot CH_2\cdot NMe_2PhCl,H_2O, $$
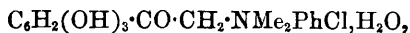
melting at 123°, and $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NMe_2PhCl$, melting at 162° with decomposition.

The following compounds have also been prepared by the author. *Paramidophenetolacetopyrogallol,* $C_6H_2(OH)_3\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot OEt$, m. p. 144°. The *chlorides,* $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot C_9NH_7Cl$, m. p. 139°, and $C_6H_2(OH)_3\cdot CO\cdot CH_2\cdot C_9NH_7Cl$, m. p. 104 from quinoline. The *chloride,* $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot C_5NH_5Cl$, m. p. 265° with decomposition, from pyridine. The corresponding base, $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot C_5NH_5\cdot OH$, obtained from the sulphate and barium carbonate, melts at 188°. The *chloride,* $C_6H_2(OH)_3\cdot CO\cdot CH_2\cdot C_5NH_5Cl$, m. p. 180°, from pyridine. *Piperidineacetocatechol,* $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot C_5NH_{10}$, m. p. 187—188°. The chloride melts at 250°.   J. W.

Thermochemical Values of the Functions of Orcinol. By DE FORCRAND (*Compt. rend.,* **118,** 284—286).—The sodium derivatives of orcinol alter rapidly when exposed to air, and also retain water or methylic alcohol even at moderately high temperatures. If ethylic alcohol is employed as the solvent, the results are not satisfactory. The monosodium derivative is best obtained by heating orcinol in a current of hydrogen with a solution of the calculated quantity of sodium hydroxide. The disodium derivative is prepared by dissolving anhydrous orcinol in absolute methylic alcohol, adding the calculated quantity of sodium, and afterwards expelling the methylic alcohol in a current of dry hydrogen. Both products are very deliquescent.

Heat of dissolution of anhydrous orcinol at $+ 10° = -2\cdot 64$ Cal.; of the monosodium derivative, $+ 8\cdot 46$ Cal.; of the disodium derivative, $+ 17\cdot 44$ Cal. Berthelot and Werner's determinations of the heats of neutralisation were confirmed. It follows that

$C_7H_6(OH)_2$ sol. $+$ Na sol. $=$ H gas $+$
$C_7H_6(OH)(ONa)$ sol. .... develops $+40\cdot 23$ Cal.
$C_7H_6(OH)(ONa)$ sol. $+$ Na sol. $=$ H gas
$+ C_7H_6(ONa)_2$ sol. .... „ $+39\cdot 13$ „
$C_7H_6(OH)_2$ sol. $+$ Na$_2$ sol. $=$ H$_2$ gas $+$
$C_7H_6(ONa)_2$ sol. .... „ $+79\cdot 36$ „

The mean value of the two functions is $+ 39\cdot 68$ Cal., a number very similar to those obtained with other phenols.   C. H. B.

Phloroglucitol. By W. WISLICENUS (*Ber.,* **27,** 357—359).—When phloroglucinol is carefully reduced by means of sodium amalgam in the cold in an approximately neutral solution, it is converted into 1 : 3 : 5-*trihydroxyhexamethylene* or *phloroglucitol,* $C_6H_{12}O_3$. This is extracted from the products of the reaction with ether, and the ethereal solution evaporated under diminished pressure. The syrup, after a time, deposits crystals of phloroglucitol, which can be purified by recrystallisation from water, or from dilute alcohol. It is thus obtained in well-developed colourless rhombohedra, which contain 2 mols. H_2O, the latter being gradually evolved in the desiccator, and completely

s 2

at 85°. When heated, it froths up at 115°, losing the water of crystallisation and again becoming solid, and on further heating the anhydrous compound melts at 184—185° and distils at about 300° almost without decomposition, if the quantity taken is small. It has a faint, purely sweet taste, and shows none of the colour reactions given by phloroglucinol.   H. G. C.

Carbamide Derivatives of Paraphenylenediamine. By H. SCHIFF and A. OSTROGOVICH (*Ber.*, **27**, 398—401).—When tolidine dihydrochloride is treated with sodium acetate, the monhydrochloride is produced without any acetyltolidine, whereas the corresponding salt of paraphenylenediamine, when boiled with aqueous sodium acetate, is converted into *acetylparaphenylenediamine hydrochloride*, $HCl,NH_2 \cdot C_6H_4 \cdot NHAc$. When this substance is treated with a second molecule of sodium acetate, no diacetyl compound is produced, but the free base is simply separated. Acetylphenylenediamine reacts with ethylic chloroformate to form *acetamidophenylurethane*, $NHAc \cdot C_6H_4 \cdot NH \cdot COOEt$, which crystallises in small, hard prisms, melting at 202·5°. It dissolves in concentrated hydrochloric acid, and is converted, by boiling with this acid, into *amidophenylurethane hydrochloride*, which is readily soluble in water and alcohol, and melts, with decomposition, at 242—244°. The free base has been previously prepared by the reduction of the corresponding nitrourethane. *Uramidophenylurethane*, $NH_2 \cdot CO \cdot NH \cdot C_6H_4 \cdot NH \cdot COOEt$, is obtained by the action of the hydrochloride on aqueous potassium cyanate. It is soluble in alcohol, insoluble in ether, and crystallises in colourless prisms, melting at 197—198°. *Di-acetylamidophenylcarbamide*, $CO(NH \cdot C_6H_4 \cdot NHAc)_2$, is prepared by fusing acetylphenylenediamine with carbamide; when the melt is extracted with dilute hydrochloric acid, it is left as a colourless, crystalline mass, which is almost insoluble in the usual solvents, and melts at 344° (corr.). The hydrochloric acid extract contains, in addition to unattacked acetylphenylenediamine, a small amount of *acetylamidophenylcarbamide*, $NHAc \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$; this is more conveniently prepared by treating the hydrochloride of acetylphenylenediamine in aqueous solution with potassium cyanate, and evaporating over sulphuric acid. It forms long, thin prisms, melting at 354° (corr.). When it is boiled with hydrochloric acid, *paramidophenylcarbamide hydrochloride*, $HCl \cdot NH_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, is produced; this crystallises in plates, is readily soluble in water, less readily in alcohol, and, when heated, decomposes without melting. The *free base* crystallises from ether in colourless plates, which become coloured on exposure to air, and melt at 129—130° (corr.).

The *acid sulphate* of *acetylamidophenylenediamine*, crystallises in small, colourless needles, which become coloured in the air, and melt at about 285°.   A. H.

Oxidation of Paraphenylenediamine. By E. BANDROWSKI (*Ber.*, **27**, 480—486).—The product of this oxidation, by means of the oxygen of the air (Abstr., 1889, 173), is now shown to have the

tripled formula $C_{18}H_{18}N_6$, probably $C_6H_4 < {}^{N \cdot C_6H_3(NH_2)_2}_{N \cdot C_6H_3(NH_2)_2} [N : (NH_2)_2$
$= 1 : 2 : 5]$. It may be obtained crystallised with $1H_2O$ in bronze coloured crystals by oxidising an ammoniacal solution of the diamine by means of a current of oxygen, or with ammoniacal potassium ferricyanide. When reduced, best with ammonium sulphide, it yields a *leuco-product*, $C_{18}H_{20}N_6$, forming small, white crystals which oxidise readily in the air, and, when heated, cake at 160°, and melt and decompose at 230°. When more strongly reduced by heating with zinc-dust, it yields paraphenylenediamine. When heated with acetic anhydride, on the water bath or in a sealed tube, it yields a *tetracetyl derivative*, $C_{18}H_{14}Ac_4N_6$, which forms long, brick-red crystals, and crystallises from 75 per cent. alcohol with $2H_2O$ in red, quadratic crystals. When this derivative is heated with phenyl-hydrazine or ammonium sulphide in alcoholic solution, it is reduced to a *leuco-product*, $C_{18}H_{16}Ac_4N_6$, which forms woolly crystals turning red in the air, crystallises with 2HCl in white crystals, and, when heated with zinc and acetic acid, loses $2H_2O$, yielding an anhydride $C_{26}H_{24}N_6O_2$. This anhydride may be obtained directly from the acetyl derivative by reduction with zinc and 75 per cent. acetic acid; it crystallises in small quadratic or rhombic plates.   C. F. B.

Diazo-compounds and Nitrosamines. By C. SCHRAUBE and C. SCHMIDT (*Ber.*, **27**, 514—523).—*Sodium paranitrophenylnitrosamine* is obtained by adding a solution of paranitrodiazobenzene chloride to a solution of sodium hydroxide heated at 50—60°. The yield is quantitative. It crystallises from 90 per cent. alcohol with $1H_2O$, and, when heated at 50—60°, loses its water of crystallisation and turns bright yellow. The corresponding *potassium*, *barium*, and *calcium* salts are obtained in a similar way to the sodium salt. These salts do not explode when heated; at 180° they remain unaltered, and gradually blacken at 250°. The diazo-derivatives of ortho- and meta-nitraniline are also easily converted into nitrosamine salts, which are, however, so soluble that they have not been separated. *Para-nitrophenylnitrosamine* is obtained as a bright yellow precipitate by acidifying an ice-cold solution of its salts with acetic acid. It is stable in ice-cold water, but when warmed decomposes with evolution of nitrogen. Sodium paranitrophenylnitrosamine is slowly converted into paranitrodiazobenzene chloride when allowed to remain with hydrochloric acid at 0°, and more rapidly at 20°; a small quantity of the diazo-amido-compound is formed at the same time. Para-nitromethylaniline is obtained when the above sodium salt is warmed with methylic iodide and methylic alcohol at 50—60°, and the nitroso-compound thus obtained is converted into the nitro-compound. The latter melts at 151°.

Potassium diazobenzene is obtained by adding diazobenzene chloride to a 67 per cent. solution of potassium hydroxide (100 parts), and warming the mixture on the water bath. The product cannot, however, be isolated, as it decomposes except in the presence of alkalis. If, however, a mixture of diazobenzene chloride and a 75 per cent. solution of potassium hydroxide is heated quickly at 130° and

finally at 140°, potassium phenylnitrosamine is obtained. It crystal-lises in silvery leaflets, and may be easily converted into monomethyl-aniline by heating with methylic iodide and methylic alcohol, and then eliminating the nitroso-group from the nitrosomethylaniline thus obtained.   E. C. R.

Benzenediazoic acid. By E. BAMBERGER (*Ber.*, **27**, 359—379; com-pare Abstr., 1893, i, 327). In a previous paper, the author has shown that the benzenediazoic acid obtained by the oxidation of diazobenzene is, in all probability, either phenylnitramine, NHPh·NO₂, or phenyl-imidonitric acid, NPh:NOOH, the former being the more probable. Further investigation has confirmed the first formula, but substances have also been obtained which appear to be derived from phenyl-imidonitric acid.

The acid is prepared in the manner already described, and with alkali metals yields salts, which crystallise in lustrous, white plates; it is decomposed by light with formation of ortho- and para-nitraniline, the latter in small quantity only. When carefully reduced with sodium amalgam in the cold, in a solution which is kept only slightly alkaline, it is converted into phenylhydrazine—aniline, ammonia, and other products being also formed. This reaction confirms the sup-position that the constitution of the acid is represented by the formula NHPh·NO₂. In further confirmation of this formula, it is found that the sodium salt, on treatment with methylic iodide in alcoholic solution, yields the *α-methyl* derivative, NPhMe·NO₂, which, on reduction, yields first phenylmethylnitrosamine,

NMePh·NO,

and then asymmetrical methylphenylhydrazine, NMePh·NH₂.

α-Methylic benzenediazoate crystallises in lustrous compact monosym-metric prisms or flat, satiny needles. melts at 38·5—39·5°, is almost odourless, volatilises in steam with very slight decomposition, and is unaffected by light. When boiled with 30 per cent. sulphuric acid, it undergoes an intramolecular change, forming *orthonitromethylaniline* and *paranitromethylaniline*. These compounds were also prepared for comparison by methylating ortho- and para-nitraniline; the former crystallises in orange-red needles having a violet shimmer, melting at 35—36°, and the latter in broad, yellow, lustrous prisms melting at 150—151°. On boiling with aqueous potash, the α-methylic salt is converted into ammonia, methylamine, aniline, and methylaniline.

If, instead of the sodium salt of benzenediazoic acid, the silver salt is treated with methylic iodide, an isomeric methylic salt is obtained, which may be termed the *β-methylic* salt; it has not yet been obtained pure, but differs very greatly from the α-derivative, having the usual properties of a diazo-compound. It is very unstable, has a pleasant heliotrope-like odour, and gives an immediate violet colora-tion with α-naphthylamine and acetic acid; when treated with mineral acids, it violently evolves gases consisting of nitrogen and its oxides, the residual solution containing aniline, methylaniline, ortho-nitraniline, paranitraniline, and small quantities of hydroxylamine and substances resembling nitrophenol.

An attempt was made to obtain a crystalline β-salt by acting on the silver salt with paranitrobenzylic chloride, but the reaction was so violent that the products were decomposed. The corresponding *α-orthonitrobenzylic* salt is readily prepared by the action of ortho-nitrobenzylic chloride on the sodium salt, and crystallises in broad, vitreous, colourless needles melting at 99·5°; when dissolved in concentrated sulphuric acid, it undergoes the usual intramolecular change, with formation of *paranitrobenzylorthonitraniline*,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot C_6H_4 \cdot NO_2,$$
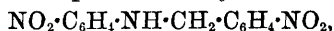
which forms golden-yellow, silky needles, and melts at 138°.

A further proof that the displaceable hydrogen atom in benzene-diazoic acid is present as an imido-group is shown by the action of bleaching powder, which converts it into the *chlorimide*, $NPhCl \cdot NO_2$; this is a dark brown oil, which, when freshly prepared, has all the properties of the chlorimides, but, on remaining, even in the dark, for 24 hours undergoes intramolecular change with formation of 4 : 2-chloronitraniline, small quantities of the isomeric 2 : 4-chloronitr-aniline being also probably formed.

The formation of phenylnitramine, $NHPh \cdot NO_2$, by the oxidation of diazobenzene is a further confirmation of the supposition that this exists in two tautomeric forms, namely, $Ph \cdot N \colon N \cdot OH$ and $NHPh \cdot NO$; in the latter form it is the first representative of the series of aromatic nitrosamines.   H. G. C.

Nitration of Aniline. By E. Bamberger (*Ber.*, **27**, 584—587; compare preceding abstract).—Benzenediazoic acid, $NHPh \cdot NO_2$, is obtained synthetically by the action of nitric anhydride on aniline in ethereal solution at −20°. The yield is 3·8 grams of crude acid from 10 grams of anhydride. In addition to benzenediazoic acid, aniline nitrate, diazobenzene nitrate, diazoamidobenzene, ortho- and para-nitraniline, and probably azobenzene are formed. The author gives full details of the methods employed for the separation and purification of these compounds, and of the tests by which they were identified. It has previously been shown how readily a nitro-group in the side chain "wanders" to the nucleus under the influence of mineral acids, and the author suggests that, in nitration, the hydrogen atom in the side chain is first replaced and that molecular rearrange-ment, caused by the excess of nitric acid, then takes place; in support of this, he refers to the ease with which hydrogen atoms in side chains react, and also to the formation of aromatic diazoamido- or amidoazo-derivatives according to the absence or presence of mineral acids.   J. B. T.

Modes of Formation of Formazyl Compounds. By H. v. Pechmann (*Ber.*, **27**, 320—322).—These compounds can be prepared

(1.) By the action of diazobenzene on phenylhydrazones, mostly in alkaline solution,

$$X \cdot CR \colon N_2HPh + OH \cdot N_2Ph \rightarrow N_2Ph \cdot CR \colon N_2HPh.$$

(2.) By the action of phenylhydrazine on phenylhydrazides, and spontaneous oxidation of the product,

$$O{:}CH{\cdot}N_2H_2Ph + N_2H_3Ph \rightarrow N_2H_2Ph{\cdot}CH{:}N_2HPh \rightarrow$$
$$N_2Ph{\cdot}CH{:}N_2HPh.$$
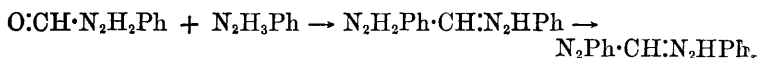
(3.) By the action of certain phenylhydrazones on phenylhydr-azine,

$$CPhCl{:}N_2HPh + N_2H_3Ph \rightarrow N_2H_2Ph{\cdot}CPh{:}N_2HPh \rightarrow$$
$$N_2Ph{\cdot}CPh{:}N_2HPh.$$
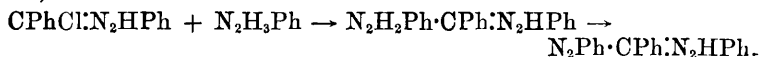
This last method has only been observed in the one instance quoted.

Benzoylchloride phenylhydrazone, obtained by the action of phosphorus pentachloride on symmetrical benzoylphenylhydrazine, forms colourless crystals melting at 131°, and is converted into formazyl-benzene when allowed to remain at the ordinary temperature with excess of phenylhydrazine in alcoholic solution.　　　　C. F. B.

Oxidation of Formazyl Compounds. By H. v. PECHMANN and P. RUNGE (*Ber.*, **27**, 323—324).—Oxidising agents cause formazyl-benzene, $NPh{:}N{\cdot}CPh{:}N{\cdot}NHPh$, to take up an atom of oxygen, yield-ing a colourless ammonium base, probably $CPh{\Big<}{\,}^{N{:}NPh{\cdot}OH}_{N{\cdot}NPh}$. The chloride and bromide of this base were analysed; they crystallise with 1 mol. of water, alcohol, or chloroform. From them, silver oxide liberates the base; this reacts strongly alkaline in aqueous solution, and is reconverted into formazylbenzene by reducing agents.

Formazyl-formic acid (hitherto called formazyl-carboxylic acid) and its ethylic salt yield analogous compounds.　　　　C. F. B.

Molecular Transformation of Oximes into Amides. By E. BECKMANN (*Ber.*, **27**, 300—315).—The author inclines to the opinion that the agents which provoke this transformation act " catalytically," causing an interchange of position between atoms or groups of atoms in the molecule, and possibly a subsequent rearrangement of the atoms. In support of this view is the fact that molecular transfor-mations are most frequently observed where a hydrogen atom or a hydroxyl group is concerned, these being just the two ions whose velocity of migration is the greatest. The agent used to induce the transformation serves to supply, from an external source, enough energy to bring about the movement of the atoms within the mole-cule. Something depends on the nature of this agent; just as, to draw an analogy, iodide of nitrogen is exploded only by sound waves of relatively great frequency. Conditions obtaining within the mole-cule also exert an influence; transformation being notoriously fa-voured by the greater relative proximity of the atoms or groups concerned, as, when they are in the " syn " position of Hantzsch, or in the " plane-symmetrical " position of Wislicenus.

For further details, reference must be made to the original paper, which it is impossible to abstract satisfactorily.　　　　C. F. B.

Synthesis of Oxanilide Dioxime. By A. F. HOLLEMANN (*Rec. Trav. Chim.*, **12**, 290—297). The author has improved Wallach's

method (*Ber.*, **12**, 1060 ; **13**, 528) of preparing dithio-oxanilide, and confirms the melting point recorded by Wallach, namely, 133°. When dithio-oxanilide is heated on the water bath with an alcoholic solution of hydroxylamine (base), oxanilide dioxime is obtained ; it appears to be identical with that prepared from dibromonitroacetonitrile (Abstr., 1893, i, 494), but melts at 210° instead of 215°.

<div align="right">A. R. L.</div>

Benzylthiocarbamides. By P. SPICA (*Gazzetta*, **23**, ii, 553—558).—The author replies to Salkowski's criticism (this vol., i, 11) of Mazzaron's work (Abstr., 1893, i, 411), and gives a short historical sketch of the subject.

<div align="right">W. J. P.</div>

Ureïdes of α-Ketone Alcohols. By H. RUPE (*Ber.*, **27**, 582—584).—By the action of potassium cyanate on amidoacetophenone hydrochloride in aqueous solution at 100°, a compound is obtained which crystallises from glacial acetic acid, or dilute hydrochloric acid, in silky, lustrous needles melting above 260°. It appears to be the ureïde of acetophenone alcohol, being formed from the carbamide by elimination of 1 mol. H_2O, and has the formula $CO{<}^{NH \cdot CPh}_{NH \cdot CH}$ or $CO{<}^{N{=}CPh}_{NH \cdot CH_2}$. The compound is soluble in dilute soda, and is reprecipitated on acidifying ; in presence of alcohol, it gives a dark-brown coloration with ferric chloride, reduces alkaline copper and ammoniacal silver solutions immediately on heating, and the latter more slowly at ordinary temperatures. The *bromo-derivative* melts at 185° with decomposition. The *acetyl-derivative* crystallises in lustrous prisms melting at 157°. The *nitro-derivative* is deposited in slender needles ; it melts at 160°, and, on treatment with soda, yields a compound crystallising in lustrous, flat needles melting at 213°. The relationship, if any, between the above compound and the one prepared by Marckwald and Ellinger from amidoacetal and carbamide (Abstr., 1892, 1326), remains undetermined. Amidocamphor, hydrochloride, and potassium cyanate yield a *carbamide derivative* which crystallises in slender, colourless needles, and melts at 169°.

<div align="right">J. B. T.</div>

Phosphazobenzene Chloride and its Derivatives. By A. MICHAELIS and G. SCHROETER (*Ber.*, **27**, 490—497).—When aniline hydrochloride is heated with phosphorus trichloride, it yields *phosphazobenzene chloride*, NPh:PCl (analogous to diazobenzene chloride, NPh:NCl, and thionylaniline, NPh:SO). This forms transparent, white crystals, melts at 136—137°, and decomposes when distilled, even under reduced pressure. It is decomposed by various reagents, yielding aniline hydrochloride, and, with water, phosphorous acid, with alcohol, ethylic phosphite, with phenol, phenylic phosphite, with hydrogen chloride, phosphorus trichloride. It reacts with various other substances enumerated below, the chlorine atom being replaced ; the products are decomposed by hydrochloric acid, yielding aniline hydrochloride, phosphorous acid, and some other compound. With

piperidine, it yields a *piperidide*, $NPh\!:\!P\cdot C_5NH_{10}$, which crystallises in long, colourless needles, and melts, when heated quickly, at 202—203°. With aniline, it yields an *anilide*, $NPh\!:\!P\cdot NHPh$ (analogous to diazoamidobenzene, $NPh\!:\!N\cdot NHPh$, and phosphenylphenylhydrazone, $PPh\!:\!N\cdot NHPh$), which forms a white, crystalline powder, melts at 152—153°, and from dilute alcohol crystallises in lustrous plates with $1H_2O$ (forming $NPh\!:\!P\cdot ONH_3Ph$?). With sodium phenoxide, it yields a *phenylic ether*, $NPh\!:\!P\cdot OPh$, which crystallises in small, lustrous prisms, and melts at 189—190°; with sodium ethoxide, an *ethylic ether*, $NPh\!:\!P\cdot OEt$, as a thick oil; and with sodium benzoxide a *benzylic ether*, $NPh\!:\!P\cdot OCH_2Ph + 2H_2O$, melting at 105°.

It has been already shown (this vol., i, 128) that with aniline hydrochloride, phosphoric oxychloride yields the compound $NHPh\cdot POCl_2$; it has since been shown that with excess of aniline hydrochloride it yields $(NHPh)_2POCl$; with free aniline, it yields $(NHPh)_3PO$. The three chlorine atoms of $POCl_3$ can thus be successively displaced by NHPh. This is not the case with phosphorus trichloride, from which, as above shown, only the compounds $NPh\!:\!PCl$ and $NPh\!:\!P\cdot NHPh$ are obtained.   C. F. B.

A New Class of Non-nitrogenous Bases containing Iodine. By C. HARTMANN and V. MEYER (*Ber.*, **27**, 426—432).—When iodosobenzene (5 grams) is dissolved in about 75 c.c. of concentrated sulphuric acid, kept cool, the solution assumes a dirty-brown colour, and does not contain iodosobenzene sulphate since it no longer liberates iodine from potassium iodide. The liquid is cautiously diluted with water at 0°, allowed to remain for two days, and then decanted from resinous deposits. It now contains the *sulphate* of a base, $OH\cdot IPh\cdot C_6H_4I$, being probably a derivative of the hypothetical base $IH_2\cdot OH$ (*iodonium hydroxide*), analogous to hydroxylamine. A similar change occurs with paraiodosotoluene. The *hydriodide*, $C_{12}H_9I_3$, separates on adding an alkali iodide to the solution of the sulphate just described, or better, to one of the base (see below) as a yellow, flocculent precipitate; it melts at 144°, decomposing into mono- and di-iodobenzene. The *hydrobromide* melts at 167—168°; the *hydrochloride* crystallises in white rosettes of needles, and melts at 200—201° with decomposition. The *nitrate* is crystalline, melts at 158—161°, and dissolves sparingly in hot water, whilst the sulphate is amorphous and dissolves readily in water. The *chromate* is a brilliant yellow precipitate. The free base was not isolated, but a solution of it is best obtained when a solution of the hydriodide is shaken with moist silver oxide; it has a strong alkaline reaction, becomes turbid when kept, and, if evaporated, is converted principally into an amorphous, gummy mass, together with a little paradi-iodobenzene.   A. R. L.

Iodonium Bases. By C. HARTMANN and V. MEYER (*Ber.*, **27**, 502—509).—*Diphenyliodonium iodide*, $I\cdot IPh_2$, is obtained by shaking equivalent quantities of iodosobenzene and iodobenzene with water and silver oxide during 3 to 4 hours. The filtrate, which contains the free base and its iodate, is reduced with sulphurous acid, and the

iodide precipitated with potassium iodide. The yield amounts to 93 per cent. of that required by theory. Lead oxide or potassium or sodium hydroxides may be substituted for the silver oxide, but the yield is then very small. The new base is also formed in small quantities in the preparation of iodosobenzene, and in converting 35 grams of benzene iododichloride into iodosobenzene, 2·5 grams of the iodide, I_2Ph_2, was obtained. The new iodide stands in the same relation to iodobenzene that trimethylsulphonium iodide does to methylic sulphide, and as tetramethylammonium iodide does to trimethylamine. It crystallises from alcohol in long, pale yellow needles, melts at 175—176° with formation of iodobenzene (of which it is a polymeride), and turns dark yellow on exposure to light. When heated, it is decomposed into 2 mols. of iodobenzene, and if the decomposition is started at one point it proceeds through the whole mass with development of heat.

Diphenyliodonium hydroxide, $OH \cdot IPh_2$, is obtained by shaking the iodide with moist silver oxide. It has a strongly alkaline reaction in aqueous solution, is stable in dilute solutions, and may be evaporated to a syrup with only partial decomposition. The *chloride*, $C_{12}H_{10}ICl$, crystallises in flat, white needles, and decomposes at 230° into chlorobenzene and iodobenzene. The *bromide* crystallises in beautiful, white needles, and, like the chloride, decomposes at 230°. The *dichromate*, $(C_{12}H_{10}I)_2Cr_2O_7$, crystallises in beautiful, orange-red leaflets, and explodes when heated. The aqueous solution of the base readily absorbs carbonic anhydride; with potassium ferrocyanide, it gives an easily soluble precipitate crystallising in yellow needles, and with potassium ferricyanide a precipitate of sparingly soluble flat, yellow needles.

Diphenyliodonium hydroxide gives a precipitate with yellow ammonium sulphide, closely resembling freshly-precipitated antimony sulphide; with sodium sulphide, a bright yellow precipitate is obtained, which quickly decomposes into iodobenzene and phenylic sulphide.

The authors point out that iodine is an eminently base-forming element, that a compound constituted from hydroxyl and the negative radicles iodine and phenyl is an alkaline base, that phenyl, which does not form ammonium and sulphonium bases, forms iodonium bases; and that the new compounds closely resemble derivatives of certain heavy metals, especially thallium. E. C. R.

Formation of Ethereal Salts of Aromatic Acids. By V. MEYER, H. GÜMBEL, and J. J. SUDBOROUGH (*Ber.*, **27**, 510—512).—The authors have determined the amount of methylic salt formed when 0·5 gram of acid dissolved in 10 c.c. of methylic alcohol is treated with dry hydrogen chloride.

Benzoic acid, ortho-, meta-, and para-toluic acids, 1 : 3 : 5-dimethylbenzoic acid and unsymmetrical trimethylbenzoic acid (obtained by the oxidation of durene with nitric acid) yield from 83—95 per cent. of the theoretical quantity of ethereal salt, whilst the isomeric trimethylbenzoic acid (mesitylenecarboxylic acid) only yields from 8—9 per cent. Symmetrical tribromobenzoic acid [$COOH : Br_3 =$

1 : 2 : 4 : 6] yields about 2 per cent. of ethereal salt, whilst the iso-meric tribromobenzoic acid [COOH : Br$_3$ = 1 : 3 : 4 : 5] yields 92—95 per cent. From these results, the authors conclude that those tri-substituted benzoic acids, which contain the substituents in the symmetrical position [1 : 3 : 5] are only converted into ethereal salts with difficulty, whereas their isomerides very easily yield ethereal salts.

The authors are engaged in the examination of the behaviour of the dibromo- and tetrabromo-acids under similar conditions. E. C. R.

Preparation of Symmetrical and Unsymmetrical Tribromo-benzoic acids. By J. J. SUDBOROUGH (*Ber.*, **27**, 512—514). The acids, which are somewhat difficult to prepare, may be obtained by the following methods.

Symmetrical tribromobenzoic acid, [COOH : Br$_3$ = 1 : 2 : 4 : 6], is obtained by diazotising tribromaniline, and gradually adding the solution to a solution of cuprous potassium cyanide heated at 90°. The nitrile thus obtained is extracted with ether, and heated with con-centrated hydrochloric acid at 200—230° for 6—7 hours. The acid crystallises in small, white needles, and melts at 187°.

Unsymmetrical tribromobenzoic acid, [COOH : Br$_3$ = 1 : 3 : 4 : 5], is obtained as follows :—2 : 5 : 4-dibromamidobenzoic acid, dissolved in dilute soda, is treated with sodium nitrite, and the mixture gradually poured into concentrated sulphuric acid, cooled with pieces of ice. The diazotised mixture is then gradually added to a boiling solution of cuprous bromide. The acid crystallises in beautiful needles, and melts at 235°. The *methylic salt* crystallises in needles, and melts at 154°. E. C. R.

Formation of Chlorobenzoic and Bromobenzoic Anhydrides By G. D. MOORE and D. F. O'REGAN (*Chem. Centr.*, 1893, ii, 938; from *Proc. Amer. Acad.*, 1893, 222—225). Working on similar lines to those by which they have already obtained anhydrides of nitrobenzoic acids the authors have obtained anhydrides by the action of phosphoric anhydride on halogen substituted benzoic acids dissolved in boiling benzene. *Orthochlorobenzoic anhydride* is easily soluble in alcohol, ether, chloroform, and benzene, sparingly in light petroleum, and crys-tallises in glistening, white needles. *Metachlorobenzoic anhydride* resembles the ortho-compound in solubility, and crystallises from benzene in yellowish-white needles. The *para-derivative* resembles the other two, and melts at 186°. *Orthobromobenzoic anhydride* crys-tallises in white, prismatic needles melting at 141° ; the *metabromo-derivative* yields similar needles melting at 97°, and the *para* compound melts at 212—213°. L. T. T.

Isomeric Octonaphthenic (Cylclohexamethylcarboxylic or Hexahydrorthotoluic) acids. By V. MARKOVNIKOFF (*J. pr. Chem.*, [2], **49**, 64—89).—*Orthoctonapthenic acid*, C$_6$H$_{10}$Me·COOH [= 1 : 2], is prepared from orthotoluic acid (b. p. 258·5—259° at 751 mm. ; m. p. 102) by a method differing only in detail from that prescribed

for the preparation of heptanaphthenic acid (Abstr., 1893, i, 93). It crystallises in needles, melts at 50—52°, boils at 241—242° (746 mm.), and dissolves sparingly in cold water, more freely in hot water, ether, chloroform, alcohol, light petroleum, and hot benzene. It is more volatile with steam than is hexanaphthenic acid. The *sodium, silver, calcium* (with $1\frac{1}{2}H_2O$), *barium*, and *zinc* salts are described; the three last are much less soluble in hot than in cold water. The *methylic* salt boils at 190° (769 mm.), and has a sp. gr. of 0·9929 at 0°/0°. Unlike the amides of most of the naphthenic acids, the *amide* of that under consideration cannot be obtained by heating the methylic -salt with aqueous ammonia, but is prepared by heating the acid with phosphoric chloride in light petroleum, and passing ammonia through the solution; it crystallises in flat, lustrous needles, melts at 180—181°, and dissolves sparingly in water. Orthomethyl-naphthenic acid is not altered when heated with anhydrous copper sulphate.

Metaoctonaphthenic acid. (Me : COOH $= 1 : 3$], from metatoluic acid, is a viscid, colourless liquid, which does not solidify at $-15°$; it boils at 245°, is slightly volatile with steam, and dissolves easily in most solvents except water. Its sp. gr. is 1·01822 at 0°/0°. The *sodium* salt is amorphous; the *calcium* salt, with $4H_2O$, is crystalline and more soluble in hot than in cold water; the *barium* and *zinc* salts are crystalline and less soluble in hot than in cold water; the *silver* salt is a pulverulent precipitate; the *methylic* salt boils at 196—197°, and has a sp. gr. of 0·97297 at 0°/0°; when heated with aqueous ammonia, it yields the *amide* which melts at 155—156°.

Paraoctonaphthenic acid, [Me : COOH $= 1 : 4$], from paratoluic acid, is a crystalline substance; it melts at 110—111°, boils at 245° with partial decomposition, sublimes in laminæ at 100°, and dissolves freely in alcohol, ether, chloroform, and light petroleum, but only -sparingly in water. The *sodium, calcium, barium, silver*, and *zinc* salts are described; the last-named is more soluble in cold than in hot water. The *methylic* salt boils at 192—194° (748 mm.), and has a sp. gr. of 0·9687 at 0°/0°; when heated with aqueous ammonia, it yields the *amide*, which melts at 220—221°.

α-Octonaphthenic acid has not been obtained from phenylacetic acid; it constitutes the main portion of the acid separated from naphtha, and its isolation is fully detailed, the principle of the operations being the fractional saturation of the acids with alkali, and the distillation of the free acid in steam. It is an oily liquid which does not solidify at $-20°$; it boils at 237—238° (750 mm.), has a sp. gr. of 1·0020 at 0°/0°, and is sparingly soluble in cold water. The *sodium, silver, calcium*, and *zinc* salts are described; the two last are more soluble in cold than in hot water. The *methylic* salt boils at 189—190° (corr.), and the *amide* melts at 128—129°. The constitution of the acid is discussed by the light of the fact that when heated with hydriodic acid it yields an octonaphthene, which is convertible into tetrabromoparaxylene; the most probable conclusion is that the acid is a stereoisomeride of metaoctonaphthenic acid; but the attachment of both CH_3 and COOH to the same carbon atom is not wholly improbable. An investigation of the lower boiling methylic salts obtained

from natural naphthenic acid is described, but no definite conclusions are stated. A. G. B.

Reduction of Salicylic acid. By A. EINHORN and R. WILLS-TÄTTER (*Ber.*, **27**, 331).—In a previous paper (this vol., i, 87), the authors stated that one of the products of the reduction of salicylic acid by sodium in amylic alcohol solution was hexahydrosalicylic acid. They now find that the substance melting at 105° is not, as they supposed, hexahydrosalicylic acid, but normal pimelic acid.

J. W.

An Isomeride of Fraxetin and its Derivatives. By P. BIGINELLI (*Gazzetta*, **23**, ii, 608—620).—*Hydroxydimethoxy-β-methylcoumarin*,

$$OH \cdot C_6H(OMe)_2 < \begin{matrix} CMe \colon CH \\ | \quad | \\ O —CO \end{matrix}$$, is prepared by the action of concentrated

sulphuric acid on a hot solution of dimethoxyquinol in ethylic aceto-acetate, or by reducing the solution with stannic chloride; the former process gives an almost theoretical yield, whilst the latter gives a somewhat smaller one. The coumarin forms tabular, colourless crystals melting at 191—191·5°; it is soluble in potash, the solution sometimes showing a ¦bluish-green fluorescence. On boiling with alcoholic potash and methylic iodide, it yields *trimethoxy-β-methyl-coumarin potassium iodide*, $(C_{13}H_{14}O_6)_2,KI$, which separates from absolute alcohol in small, yellowish, monosymmetric prisms, $a : b : c = 0·5942 : 1 : 0·3658$; $\beta = 85° 48'$, and decomposes at 220°. *Tri-methoxy-β-methylcoumarin* is obtained on treating this double compound with hot water; it forms long, monosymmetric needles, $a : b : c = 0·9187 : 1 : 1·2551$; $\beta = 84·19°$, melts at 116—117°, is very soluble in alcohol, and is found to contain three methoxy-groups by Zeisel's method.

Trihydroxy-β-methylcoumarin, $C_6H(OH)_3 < \begin{matrix} CMe \colon CH \\ | \quad | \\ O —CO \end{matrix}$, is prepared by

heating the preceding substance with hydriodic acid, methylic iodide being simultaneously formed; it crystallises in minute scales, melts at 244—246°, and yields the above methoxy-derivative on methyla-tion. If excess of concentrated hydriodic acid is used in its prepara-tion, a *substance*, $C_{19}H_{18}O_9$, is obtained, which forms white, anorthic scales melting at 253—254°; $a : b : c = 0·483 : 1 : 0·622$; $a = 95° 13'$; $\beta = 107° 14'$; $\gamma = 101° 41'$. The author assigns to this the following constitution:—

$$\begin{matrix} C_6H(OH)_4 \cdot CMe \cdot CMe \cdot C_6H(OH)_3 \\ | \qquad \qquad | \\ CH_2 —CH ———CO \end{matrix} > O.$$

On heating trimethoxy-β-methylcoumarin with excess of alcoholic potash and methylic iodide under given conditions, the *methylic* salts of two *tetramethoxy-β-methylcinnamic acids*,

$$C_6H(OMe)_4 \cdot CMe \colon CH \cdot COOH,$$

are obtained. The methylic salt which is least soluble in light petroleum, forms lustrous, monosymmetric prisms; $a : b : c = 0·6045 : 1 : 0·4590$; $\beta = 56° 29'$; it melts at 77·5—78°. The corre-sponding acid is obtained in monosymmetric prisms; $a : b : c = 1·7223 : 1 : 2·3075$; $\beta = 57° 23'$; this melts at 148—149°, and

when dissolved in alkali carbonates, and reprecipitated with hydrochloric acid it is partially converted into the isomeric acid described below.

The second methylic salt crystallises in needles melting at 67—68°; the acid from which it is derived forms anorthic crystals; $a : b : c = 0·7217 : 1 : 0·8834$; $\alpha = 100° 37'$; $\beta = 101° 29'$; $\gamma = 61° 15'$. It may be partially converted into the isomeric acid by heat or by treatment with mineral acids. The author is still engaged with the investigation of these acids. W. J. P.

Norhemipinic acid. By M. FREUND and F. HORST (*Ber.*, **27**, 332—339).—Hemipinic acid (1 mol.), when heated with phosphorus pentachloride (5 mols.) for five hours at 170—175°, gives a yellow liquid, which decomposes when poured into water, yielding an oil which crystallises after a time. The crystals, when washed with ether and recrystallised from benzene, are colourless and melt at 166°. The substance is *orthodichloromethoxyphthalic anhydride,*

$$C_6H_2(O·CH_2Cl)_2 {<}^{CO}_{CO}{>}O \; [= 1 : 2 : 3 : 4].$$
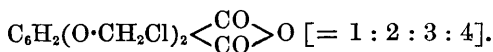
On boiling with water, it yields formaldehyde, hydrogen chloride, and norhemipinic acid. A crystalline product obtained in another experiment proved to be *hydroxychloromethoxyphthalic anhydride,*

$$CH_2Cl·O·C_6H_2(OH){<}^{CO}_{CO}{>}O \; [= 1 : 2 : 3 : 4],$$
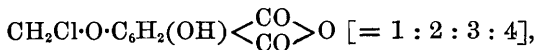
melting at 130—135°.

Norhemipinic acid, $C_{10}H_{10}O_6 + H_2O$, is obtained directly from the product of the interaction of hemipinic acid and phosphorus pentachloride by pouring it into water and digesting for several hours on the water bath. The filtered solution is then boiled for some time, treated with animal charcoal, and evaporated to crystallisation. The acid is purified by again boiling with animal charcoal, and precipitating with concentrated hydrochloric acid. To obtain it in the perfectly pure condition, it must be prepared from the pure ammonium or barium salt. It crystallises from water in long, narrow, colourless, rhombic plates or in thick, rhombic prisms, containing $1H_2O$, which is lost at 105°, leaving the anhydrous acid, this melts at 210—212°, decomposing into the anhydride and water. It dissolves easily in alcohol and in hot water, and is almost insoluble in ether, benzene, and light petroleum.

The *ammonium* salt is anhydrous and melts at 202° with decomposition. Its solutions give precipitates with silver, barium, calcium, cupric, ferric, and lead salts. On careful addition of acid, the *ammonium hydrogen* salt, $C_8H_5O_6NH_4 + H_2O$, may be precipitated. The *barium* salt, with $2H_2O$, and *calcium* salt, with $3H_2O$, are described.

When the anhydrous acid is heated for one hour at 205—210°, it changes into a brownish mass, which, when dissolved in alcohol and precipitated with water, yields the *anhydride,* $C_8H_4O_5 + 2H_2O$, melting at 238°. The anhydride is soluble in much hot water, giving a solution with a splendid green fluorescence; it is insoluble in

benzene. No fluorescein is obtained on heating it with resorcinol. It is strongly acid, and gives a barium salt, $(C_8H_3O_5)_2Ba + 4H_2O$.

<div align="right">J. W.</div>

Mercury Derivatives from Dimethylaniline. By L. PESCI (*Gazzetta*, **23**. ii, 521—529; compare Abstr., 1893, i, 24).—Yellow mercuric oxide dissolves readily in an aqueous solution of dimethylaniline acetate, and separation of *paramercurodiphenylenetetramethyl-mercurodiammonium acetate,* $Hg{<}{C_6H_4 \cdot NMe_2(OAc) \atop C_6H_4 \cdot NMe_2(OAc)}{>}Hg$, occurs; it is obtained in thin needles melting at 162°, is soluble in benzene, chloroform, acetic acid or boiling alcohol, but insoluble in water. It yields the *hydroxide* on treatment with caustic potash; this crystallises in microscopic prisms, melts at 179°, and is very sparingly soluble in cold water, giving a feebly alkaline solution. The *chloride* separates from boiling alcohol in lustrous, colourless laminæ; it is soluble in boiling benzene but not in water, and is changed by light.

On boiling the hydroxide described above with methylic iodide, *paramercurodimethylaniline methiodide,* $Hg(C_6H_4 \cdot NMe_3I)_2$, is obtained; it crystallises from boiling water in very thin, flexible needles melting at about 230°. It is not attacked by boiling potash, and is soluble in boiling alcohol. On treatment with siver oxide, it yields *paramercuro-diphenylenehexamethyldiammonium hydroxide,* $Hg(C_6H_4 \cdot NMe_3 \cdot OH)_2$, as a caustic liquid, which rapidly absorbs carbonic anhydride. The *chloride* crystallises in small, thin needles, and is soluble in water and in alcohol; with mercuric chloride, it yields a double *salt,* which crystallises in laminæ and melts at 225° with decomposition.

Paramercurodimethylaniline methiodide yields trimethylphenylammonium iodide on reduction with sodium sulphide; the hydroxide, on similar treatment, gives paramercurodimethylaniline. The latter, when heated with methylic iodide, yields paramercurodimethylaniline methiodide. On treating an alcoholic solution of paramercurodi-phenylenehexamethylammonium chloride with bromine, parabromo-trimethylphenylammonium chloride is obtained. These reactions prove the constitution of the compounds described above.

<div align="right">W. J. P.</div>

Constitution of Mercurophenylamine and of Methylphenyl-mercurammonium Hydroxide. By L. PESCI (*Gazzetta*, **23**, ii, 529—533).—The base, which the author has previously described as mercurophenylamine (Abstr., 1892, 1448), yields paramercurodi-methylaniline methiodide on boiling with methylic alcohol and methylic iodide; mercurophenylamine, therefore, has the constitution $Hg{<}{C_6H_4 \cdot NH \atop C_6H_4 \cdot NH}{>}Hg$, and the name must, consequently, be changed to paramercurodiphenylenemercurodiamine.

Methylphenylmercurammonium hydroxide, on treatment with methylic iodide, yields a crystalline product, which gives paramer-curodimethylaniline methiodide and mercuric sulphide on the addition of barium sulphide. The hydroxide, therefore, has the constitution

$$Hg<\genfrac{}{}{0pt}{}{C_6H_4\cdot NHMe(OH)}{C_6H_4\cdot NHMe(OH)}>Hg,$$ and should be termed *paramercurodiphenylenedimethylmercurodiammonium hydroxide*.

Paramercuroaniline, $Hg(C_6H_4\cdot NH_2)_2$, is prepared by heating paramercurodiphenylenemercurodiamine with sodium sulphide on the water bath; it is extracted from the product by chloroform, and is ultimately obtained in yellowish needles melting at 174° with decomposition.

Paramercuromethylaniline, $Hg(C_6H_4\cdot NHMe)_2$, is obtained by the action of sodium sulphide on paramercurodiphenylenedimethylmercurodiammonium hydroxide; it separates from its benzene solution in lustrous, colourless needles melting at 178—179°, and is sparingly soluble in alcohol. W. J. P.

Mercury Derivatives from Diethylaniline. By A. PICCININI (*Gazzetta*, **23**, ii, 534—543).—The author has prepared a number of aromatic mercury-derivatives from diethylaniline analogous to those obtained by Pesci (see preceding Abstract) from dimethylaniline.

Paramercurodiphenylenetetrethylmercurodiammonium acetate,

$$Hg<\genfrac{}{}{0pt}{}{C_6H_4\cdot NEt_2(OAc)}{C_6H_4\cdot NEt_2(OAc)}>Hg,$$
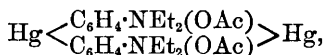
crystallises in long, colourless needles melting at 104·4°. The *hydroxide* is obtained in colourless needles melting at 200° with decomposition; it has a strongly alkaline reaction, and is slowly decomposed by boiling water. The *chloride* forms thin, colourless needles melting at 164·5°, and is sparingly soluble in hot water.

Paramercurodiethylaniline methiodide, $Hg(C_6H_4\cdot NEt_2MeI)_2$, crystallises in colourless prisms, melting at 202·8° with decomposition, and is very soluble in boiling water; the *methoxide* was only obtained in aqueous solution. The *methochloride* crystallises in thin, colourless, deliquescent needles, and forms a double *salt* with mercuric chloride, which separates from boiling water in lustrous laminæ, melting at about 200° with decomposition.

On reducing the preceding methiodide with sodium sulphide, a salt of diethylmethylphenylammonium is obtained.

On reducing parabromodiethylaniline with sodium amalgam, *mercurodiethylaniline*, $Hg(C_6H_4\cdot NEt_2)_2$, is produced; it crystallises from benzene in colourless, efflorescent prisms, melting at 160·6°. The constitution of paramercurodiethylaniline methoxide is proved by the fact that it yields the same mercurodiethylaniline on reduction with sodium sulphide. W. J. P.

Mercury Derivatives from Ethylaniline. By G. RUSPAGGIARI (*Gazzetta*, **23**, ii, 544—548; compare preceding Abstracts).—*Paramercurodiphenylenediethyldiammonium acetate*,

$$Hg<\genfrac{}{}{0pt}{}{C_6H_4\cdot NHEt(OAc)}{C_6H_4\cdot NHEt(OAc)}>Hg,$$
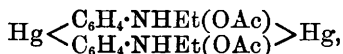
separates from a solution of mercuric acetate in an alcoholic solution of ethylaniline; it crystallises in colourless, transparent prisms,

and melts at 130°. It is insoluble in cold water, and is decomposed by hot water. On treatment with potash, it yields the *hydroxide*, which crystallises in beautiful, colourless needles, decomposing at 145°; this is soluble in hot water, giving a strongly alkaline solution. The *chloride* separates from alcohol in lustrous, six-sided laminæ, melting at 142°, and is decomposed by boiling water. On heating the base with methylic alcohol and methylic iodide in a reflux apparatus, it yields *paramercurodiphenylenetetramethyldiethyldiammonium iodide*, $Hg(C_6H_4 \cdot NEtMe_2I)_2$, which crystallises in long, colourless needles melting at 202°. On treating its aqueous solution with silver chloride, the corresponding *chloride* is obtained in long, colourless needles, very soluble in water. With mercuric chloride, it forms a double *compound*, which melts at 169°.

Mercuroethylaniline, $Hg(C_6H_4 \cdot NHEt)_2$, is obtained by reducing paramercurodiphenylenediethylmercurodiammonium hydroxide with sodium sulphide. It crystallises in lustrous laminæ, melting at 166°. W. J. P.

Derivatives of Disulphobenzoic acid [1 : 3 : 5]. By K. Hopf-gartner (*Monatsh.*, **14**, 685—698).—*Disulphobenzoic trichloride*,

$$C_7H_3O_5S_2Cl_3,$$

is obtained by heating dry potassium disulphobenzoate, $C_7H_3O_8S_2K_3$, with phosphoric chloride in an oil bath at 150°. A better yield is obtained by heating the mixture in sealed tubes in a bath of amylic alcohol. From benzene, it crystallises with 1 molecule of the solvent in large, colourless prisms. When free from benzene, it melts at 86·5—87° (uncorr.). The *salt*, $C_7H_4O_8S_2K_2 + 3H_2O$, is obtained from the crude melt, after the trichloride has been extracted with benzene, by crystallising the residue from water; it forms yellowish, flat prisms.

Disulphobenzoic dichloride, $C_7H_4O_6S_2Cl_2$, is obtained by allowing the trichloride to remain with water for some time at the ordinary temperature. It is a white, crystalline powder, softens at 180°, melts at 183° (uncorr.), and is easily dissolved in dilute soda solution, and by shaking with barium carbonate and water.

The *amide*, $C_7H_9O_5S_2N_3$, obtained by treating with dry ammonia the trichloride dissolved in benzene, crystallises in long, thin, lustrous, white needles, begins to give off ammonia at 230°, and melts at 290°. The *trianilide*, $C_{25}H_{21}O_5S_2N_3$, obtained by treating the trichloride with aniline, is a white, crystalline powder, and melts at 222° (uncorr.).

Sulphohydroxybenzoic acid, $C_7H_6O_6S$, is obtained by warming the tripotassium disulphobenzoate with a solution of potassium hydroxide at 160—165°, and is purified by means of the lead salt. It forms white crusts of microscopic needles, containing $1H_2O$, begins to decompose at 100°, but does not melt at 180°, is very hygroscopic, has a strongly acid reaction, and gives a faint reddish-brown coloration with ferric chloride. The *lead salt*, $C_7H_4SO_6Pb + 3\frac{1}{2}H_2O$, crystallises in slender, white, lustrous needles, and decomposes before it

melts. The *potassium* salt, with $3H_2O$, crystallises in small, colourless prisms.

Dihydroxybenzoic acid [1 : 3 : 5] is obtained by heating the potassium salt of disulphobenzoic acid with potassium hydroxide at 250—260°. E. C. R.

Formation of Substituted Benzophenones. By G. D. MOORE and D. F. O'REGAN (*Chem. Centr.*, 1893, ii, 938; from *Proc. Amer. Acad.*, 1893, 226—233).—Kollarits and Merz showed (this Journal, 1872, 707; and 1873, 1035) that by heating benzoic acid or anhydride with benzene and phosphoric anhydride, benzophenone is formed. Employing this reaction with their substituted benzoic anhydrides (this vol., i, 244) the authors obtained orthonitrobenzophenone, *meta-nitrobenzophenone*, melting at 94—95°, *paranitrobenzophenone*, melting at 137—138°, and ortho-, meta-, and para-chloro-, and meta- and para-bromo-benzophenones. L. T. T.

Isostilbene. By V. REDZKO (*J. Russ. Chem. Soc.*, 25, 297—298).—When isostilbene, $CPh_2:CH_2$, is treated with fuming hydriodic acid at the ordinary temperature, a solid, crystalline substance is formed, which melts at 143°, has the empirical formula C_7H_6, and is in all probability a polymeride of isostilbene. Gaseous hydrogen iodide, as well as strong sulphuric acid, also produces it at the ordinary temperature. If the fuming hydriodic acid is made to act slowly on isostilbene at the temperature of a good freezing mixture, diphenylethane (b. p. 272·5—273°) is formed, along with small quantities of the solid melting at 143°.

When bromine and isostilbene, both dissolved in light petroleum, are allowed to react in a freezing mixture, the bromide, $CPh_2Br·CH_2Br$, is obtained in colourless prisms, which may be dissolved in boiling light petroleum without decomposition. At its melting point, about 65°, the dibromide decomposes with evolution of hydrogen bromide. Even at the ordinary temperature, hydrogen bromide is given off slowly, the dibromide first melting and a solid being afterwards formed, which, from its melting point and crystalline form, was proved to be diphenylbromethylene, $CPh_2:CHBr$.

Alcohol acts on the dibromide at the ordinary temperature with formation of a crystalline compound melting at 98—99°. This substance is an ethoxybromodiphenylethane, the ethoxyl group being probably attached to the carbon atom which is united to the two phenyl groups. J. W.

Derivatives of Naphthyl Ethyl Ether. By P. HEERMANN (*J. pr. Chem.*, [2], 49, 130—134).—1 : 4-*Ethoxynaphthalenesulphonic acid*, $OEt·C_{10}H_6·SO_3H$, is very easily formed by sulphonating α-naphthyl ethyl ether with strong sulphuric acid. It is soluble in water, as is also its *sodium* salt, which, however, is insoluble in salt solution. 2 : 3'-*Ethoxynaphthalenesulphonic acid* is equally easily prepared; its *sodium* salt is sparingly soluble in water. Both compounds lose ethyl and become naphtholsulphonic acids when treated with anhydrosulphuric acid. A. G. B.

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Isomeric Nitrochloronaphthalenesulphonic acids. By P. T. CLEVE (*Chem. Centr.*, 1893, ii, 919—920; from *Öfvers K. Svenska Vet. Ak. Förh.*, 1893. 329).—As the result of his experiments on substituted naphthalenes, the author gives the following rules of substitution as trustworthy, except in such cases as clearly depend on a secondary rearrangement of the very mobile SO_3H group. (1) If the α- (or 1-) position is occupied by OH, NH, COMe, NH_2, Cl, or Br, the new radicle will enter the position 2 or 4 (occasionally 4'). (2) If the α-position is occupied by CN, NO_2, SO_3H, or COOH, the new radicle will enter the position 4' or 1' (occasionally 4). (3) If the β- (or 2-) position is occupied by OH, NH, or COMe, the new radicle will enter the position 1. (4) If the β-position is occupied by NH_2, Cl, Br, I, or SO_3H, the new radicle will enter the position 4' or 1'. (5) The group SO_2Cl in the α- or β-position predisposes the entry of the NO_2 group into an α-position of the second ring.

The following table summarises the properties of the derivatives of the 14 nitrochloronaphthalenesulphonic acids which the author has obtained.

Constitution.	Chloride.	Amide.	Ethyl salt.	Constitution.	Chloride.	Amide.	Ethyl salt.
	m. p.	m. p.	m. p.		m. p.	m. p.	m. p.
1 : 2 : 4'	112°	214°	110°	1 : 4' : 1'	150°	233°	—
1 : 2 : 3'	161	203	139	1 : 1' : 4 } ?	134	—	—
1 : 2 : 2'	219	247	184	1 : 4 : 1' }			
1 : 2 : 1'	190	226	181	1 : 1' : 2	129	245	124°
1 : 4 : 3'	116° (108°)	208	89	1 : 1' : 4'	127	181	—
1 : 4 : 2'	161°	188	123	2 : 1 : 4'	118	220	—
·1 : 4' : 3'	151	220	116	2 : 1' : 2'	182	231	—
1 : 4' : 2'	130	188	—		—	—	—

Of the 33 possible trichloronaphthalenes, 16 have been obtained by the author and others, their melting points being as follows :— 1 : 2 : 3 = 81°, 1 : 2 : 4 = 92°, 1 : 2 : 4' about 76°, 1 : 2 : 3' about 91°, 1 : 2 : 2' about 80°, 1 : 2 : 1' = 83°, 1 : 3 : 4' = 103°, 1 : 3 : 3' = 80°, 1 : 3 : 2' = 113°, 1 : 3 : 1' about 88°, 1 : 4 : 2' about 60°, 1 : 4 : 1' = 131°, 1 : 3' : 2' = 109·5°, 2 : 3' : 2' = 91°. Summaries of the properties and derivatives of the known dichloronaphthalenesulphonic acids, and of the mono- and di-chloronaphthalenes are also given.

L. T. T.

Orientation in the Terpene Series. By A. v. BAEYER (*Ber.*, 27, 436—454).—In the opening portion of this paper, the author deals with the nomenclature of the terpene series, which he models according to the rules agreed on at the Geneva Conference. The carbon atoms in cymene are thus numbered.

$$\overset{9}{\underset{10}{\text{C}}} > \text{C·C} < \overset{5}{\underset{3}{\text{C·C}}} \overset{6}{\underset{2}{\text{C·C}}} > \overset{}{\underset{}{\text{C·C}}} \, 1 \, 7$$

Wallach considers that dipentene is Δ 1 : 5-terpadiene (dihydrocymene) on the ground of its optical activity, this being the only possible configuration containing an asymmetrical carbon atom; on

this assumption, however, he is compelled to admit that intramolecular change takes place when the hydrocarbon enters into combination with halogen hydrides. The author shows that when Wallach's terpineol dibromide (this vol., i, 44) is treated with a solution of hydrogen bromide in glacial acetic acid, 1 : 2 : 4-tribromoterpane (-hexahydrocymene) is produced, which, on bromination, is converted into dipentene tetrabromide (m. p. 124°). As the bromination is carried out in the cold, intramolecular change is inconceivable; it follows, therefore, that dipentene has not the constitution assigned to it by Wallach (see below).

When the tribromide (m. p. 110°) which Wallach obtained by brominating 1 : 4-dibromoterpane (-hexahydrocymene) is dissolved in glacial acetic acid, and treated at 0° with zinc dust, it yields a *terpenol* (terpineol) *acetate*, $C_{10}H_{17}OAc$, which forms a *dibromide* melting at 103°, and is converted, on hydrolysis with alcoholic potash, into a crystalline *terpenol* (terpineol) melting at 69—70°; the latter forms a *dibromide* melting at 114—115°. Both the terpenol and its acetate, if treated with a solution of hydrogen bromide in glacial acetic acid, yield *trans-* 1 : 4-*dibromoterpene (dipentenedihydrobromide)*, melting at 64°. If the dibromide of the terpenol, or its acetate, is treated with hydrogen bromide in glacial acetic acid solution, Wallach's 1 : 4 : 8-tribromoterpane (m. p. 110°) is obtained. The terpenol acetate, like tetramethylethylene, forms a blue crystalline *nitrosochloride* (compare Thiele, this vol., i, 217), melting at 80°. These facts indicate that the new terpenol has the constitution, $OH \cdot CMe \! < \! {}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2} \! > \! C \! : \! CMe_2$. When the terpenol acetate is boiled with quinoline, terpinolene is obtained; terpinolene is, therefore, $\Delta^{1,4(8)}$-*terpadiene*, $CMe \cdot C \! < \! {}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2} \! > \! C \! : \! CMe_2$.

Dipentene is formed by the dehydration of solid terpenol (terpineol; this vol., i, 45), and the author finally concludes that it is $\Delta^{1,3}$-terpadiene (dihydrocymene). Dipentene is, however, a racemic compound of two enantiomorphous substances, and is the first instance brought to light of such a compound not containing an asymmetrical carbon atom. The author also adduces evidence that the high-boiling terpinene is $\Delta^{1,5}$-terpadiene, and the low-boiling terpinene, $\Delta^{3,5}$-terpadiene.　　　　A. R. L.

Rose Oil. By J. BERTRAM and E. GILDEMEISTER (*J. pr. Chem.*, [2], **49**, 185—196).—Monnet and Barbier (this vol., i, 141) state that they obtained rhodinol from geranium oil. The authors cannot isolate any rhodinol from the various commercial geranium oils. A reinvestigation of genuine rose oil shows that the geraniol from this source is identical with that from all other known sources. The variations in the sp. gr. of samples of geraniol are attributable to the ease with which the oil oxidises. A comparison of the properties and behaviour of the so-called rhodinol leads to the conclusion that this substance is a mixture consisting, for the most part, of geraniol, just as Barbier's licarhodol (Abstr., 1893, i, 545) is an impure geraniol. What the impurity in geraniol which lends it the odour of roses may be

has yet to be settled. In spite of the statements of Markovnikoff and Reformatzky, stearoptene must still be regarded as a mixture of hydrocarbons. A. G. B.

Essential Oil of Lemon. By R. S. LADELL (*Chem. News*, **69**, 20—21).—By fractional distillation of terpeneless oil of lemon, which is a mixture of several oxygenated compounds, the author has isolated a liquid having a constant composition approximating empirically to $C_{10}H_{18}O$, with a sp. gr. 0·962, and a specific rotatory power $[\alpha]_D = +6·42°$; it boils at 206°. D. A. L.

Campholene. By GUERBET (*Compt. rend.*, **118**, 286—288).—Delalande's process of obtaining campholene by the action of phosphoric anhydride on campholic acid does not give a good yield. The best method is to distil campholic chloride in presence of a small quantity of phosphoric anhydride, when about 73 per cent. of the calculated quantity is obtained, and a single fractionation yields a pure product.

Campholene is a colourless liquid with a burning taste, and an odour similar to that of terebenthene; it boils at 134° under a pressure of 758 mm.; sp. gr. at 0° = 0·8115; vap. density, 4·26 (calc. 4·28). It is optically inactive, and when exposed to air slowly absorbs oxygen. Bromine attacks campholene violently at 0° with evolution of hydrogen bromide, but if the two substances are previously dissolved in 10 times their weight of chloroform, the bromine is absorbed quietly, and the absorption ceases when the two substances have been mixed in molecular proportion. There is practically no evolution of hydrogen bromide, but the product is very unstable, and gives off hydrogen bromide when the chloroform is evaporated. When treated with gaseous hydrogen iodide at 0°, campholene yields a crystalline compound, C_9H_{16},HI, which is very unstable.

When heated in sealed tubes at 280° with twice its volume of hydriodic acid saturated at 0°, campholene yields a hydrocarbon, C_9H_{18}, which boils at 132—134°; sp. gr. at 0° = 0·783; vap. density 4·35. It does not combine with bromine, and is not attacked in the cold by fuming sulphuric acid or fuming nitric acid, but when heated for 10 days at 60—70° with a mixture of 2 vols. of fuming sulphuric acid and 1 vol. of fuming nitric acid, it yields a small quantity of a crystalline nitro-derivative with the same melting point as trinitropseudocumene. When treated with bromine in presence of aluminium bromide, it yields tribromopseudocumene.

It follows that the hydrocarbon, C_9H_{18}, is identical with the hexahydropseudocumene found in Baku petroleum, and, therefore, the campholene from which it is obtained must be regarded as tetrahydropseudocumene.

When sulphuric acid is agitated with one-third its weight of campholene, it rapidly blackens, and gives off sulphurous anhydride with development of heat. The products are the hexahydropseudocumene described above, and *dicampholene*, $C_{18}H_{32}$, an oily liquid which boils at 165—168° under a pressure of 30 mm., or, with partial decomposi-

tion, at 266—270° under ordinary pressure. It has an odour similar to that of terebenthene, and when exposed to air, oxidises somewhat rapidly with formation of resinous products.

It would seem that the compound obtained by Étard by the action of zinc chloride on α-chlorocamphor (Abstr., 1893, i, 524) cannot be campholene. C. H. B.

Synthetic Borneols. By G. BOUCHARDAT and J. LAFONT (*Compt. rend.*, **118**, 248—250).—Borneols of camphene are readily prepared by acting on the camphene with an equal weight of glacial acetic acid, in which has been dissolved one-third of its weight of sulphuric acid. The reaction proceeds quietly, but is almost instantaneous, and the conversion into borneol acetates is practically complete. A small quantity of a new compound is also formed, and is under investigation.

Camphene borneols form smaller crystals, and are more soluble in light petroleum than natural borneols or the borneols of terebenthene. The crystals sublime in the same way as camphor, but the borneols of terebenthene do not. Moreover, camphene borneols decompose into camphene and water if heated at 250° for 24 hours, and the decomposition is well marked, even at 225°, whereas terebenthene and dryabalanops borneols do not change under these conditions. It follows that the camphene borneols are isomeric with natural borneols, with those obtained from terebenthene, and with those having an unstable reversible rotatory power obtained by Montgolfier. On the other hand, when oxidised, they yield camphors identical with those from the other borneols.

In view of the large number of isomerides of compounds yielding identical derivatives, the authors consider that it is better to distinguish the different borneols according to their origin; for instance, camphene borneol, terebenthene borneol, rather than by such prefixes as iso, para, &c. C. H. B.

Constitution of Cotoïn. By G. CIAMICIAN and P. SILBER (*Ber.*, **27**, 409—426; compare Abstr., 1893, i, 718; this vol., i, 40, 51, 94). —Cotoïn, one of the constituents of the true Coto bark, has the formula $C_{14}H_{12}O_4$, and not $C_{22}H_{18}O_6$, as given by Jobst and Hesse. The diacetate, similarly, has the formula $C_{18}H_{16}O_6$, and, like cotoïn itself, contains a methoxy-group. When cotoïn is warmed with strong sulphuric acid, decomposition occurs, and a small amount of phloroglucinol is formed. This fact, and the general resemblance of cotoïn to hydrocotoin (Abstr., 1891, 578), renders it probable that cotoïn is the monomethyl ether of benzoylphloroglucinol, $OMe \cdot C_6H_2(OH)_2 \cdot COPh$.

Dibromocotoin, $C_{14}H_{10}Br_2O_4$, was described by Jobst and Hesse as tribromocotoïn. It forms large, prismatic, colourless needles, and melts at 116°. *Cotoinoxime*, $C_{14}H_{13}NO_4$, is obtained by adding hydroxylamine hydrochloride to a solution of cotoïn in cold aqueous sodium carbonate. It crystallises in plates, with a faint blue surface lustre. It is soluble in alcohol, slightly in water, readily in caustic alkalis. When cotoïn is treated with methylic iodide, it yields a *dimethylcotoïn*, $OH \cdot C_6HMe(OMe)_2 \cdot COPh$, isomeric with the trimethylbenzoylphloro-

glucinol (dibenzoylhydrocoton) obtained by treating hydrocotoïn in the same manner. It separates from alcohol in crystals, melting at 138°. It forms yellow solutions in aqueous alkalis, and its solution in dilute alcohol gives a yellowish-brown coloration with ferric chloride. It only contains two methoxy-groups, and has, therefore, the constitution given above. Its *acetate* crystallises in white needles melting at 150°. It is insoluble in alkalis, and gives no coloration with ferric chloride.

It still remains to determine the relative positions of the methoxy- and benzoyl-groups in cotoïn.

When cotoïn is treated with acetic anhydride, the diacetate is accompanied by another compound, which forms lustrous prisms, melting at 142°. This substance is *methoxyhydroxyphenylcoumarin acetate*, $OMe \cdot C_6H_2(OAc) < ^{O-CO}_{CPh:CH}$; it is soluble in alcohol, but insoluble in alkalis, and, when hydrolysed, yields *methoxyhydroxyphenylcoumarin*, $OMe \cdot C_6H_2(OH) < ^{O-CO}_{CPh:CH}$. The latter melts at 207°, and dissolves readily in alkalis. When this compound, or its acetate melting at 142°, is boiled with hydriodic acid, metadihydroxyphenylcoumarin, $C_6H_2(OH)_2 < ^{O-CO}_{CPh:CH}$, is obtained, melting at 233—234°, and being identical in every respect with the substance prepared synthetically by Kostaneoki and Weber (this vol., i, 88). The methoxyhydroxyphenylcoumarin is not contained in the original cotoïn, but is formed from it by condensation with acetic acid.

The authors propose shortly to publish the results of their investigation of the so-called dicotoïn. A. H.

Constitution of Santonin. By S. CANNIZZARO (*Ber.*, **27**, 530—536).—A polemical paper in answer to Klein.

Vitin and the Wax Compounds of American Grapes and their Hybrids. By W. SEIFERT (*Monatsh.*, **14**, 719—738).—The grape berries, separated from the stalks, are treated with chloroform at the ordinary temperature for 2 to 8 days, and the chloroform extract is then separated from the juice and evaporated to dryness. The residue is extracted with water and then with absolute alcohol. It is thus separated into three substances : (1) soluble in cold alcohol; (2) soluble in hot alcohol but not in cold ; (3) insoluble in alcohol.

Vitin crystallises from the cold alcoholic solution, when it is allowed to remain for some time. It is a white substance, crystallises in slender needles, and has no characteristic taste or odour. It is soluble in most organic solvents, dissolves in alkalis and sodium carbonate, and is reprecipitated by acids. It sinters, darkens, and then melts at 250—255°. The specific rotation $[\alpha]_D = +59.87$. The alcoholic solution has an acid reaction. Dilute acids have no action on the compound. It is partially dissolved by concentrated sulphuric acid, with an orange-red coloration, and is precipitated unchanged on

dilution. Concentrated nitric acid converts it into a resinous mass, which gives a deep red-brown solution with potassium carbonate, and has an intensely bitter taste. When heated with a small quantity of acetic anhydride, and then treated with concentrated sulphuric acid, a purple-red solution is obtained; the absorption spectrum of this solution shows a strong extinction between E and b, whilst the orange-red solution in sulphuric acid alone shows a dark band in the green between D and E and a continuous extinction from F into the blue and violet. If only a few drops of sulphuric acid are added to vitin which has been treated with acetic anhydride, a deep bluish-violet solution is obtained, which shows a faint extinction between C and D and a broad band at E. The author gives a table, showing the absorption spectra of vitin, abietic acid, and urson. The analysis and molecular weight determinations agree with the formula $C_{20}H_{31}O \cdot OH$. The *acetyl compound*, $C_{20}H_{31}O_2Ac$, crystallises in long needles, and sinters, darkens, and then melts at 239°. The *ammonium salt*, $C_{20}H_{31}O_2 \cdot NH_4, C_{20}H_{32}O_2$, crystallises in long needles. The *calcium salt* crystallises in long, slender needles, the *copper salt* is a bright blue powder consisting of microscopic needles. The *silver salt* is soluble in ether. Vitin does not reduce alkaline silver solution, and gives a negative result when tested for methoxyl by Zeisel's method. Therefore it contains neither an aldehyde- nor a methoxy-group.

An examination of those products obtained from the chloroform extract, which are insoluble in cold alcohol, showed that they contained wax-like compounds. The product, soluble in hot alcohol, melted at 69—70°, and contained myricyl alcohol and a fatty acid, melting at 75—80°, which, on analysis, gave numbers agreeing with the formula for cerotic or melissic acid. The product, insoluble in hot alcohol, melted at 72°, and contained an alcohol melting at 79°, and a fatty acid melting at 60—79°. E. C. R.

Brazilin. By C. SCHALL (*Ber.*, **27**, 524—530).—The author has already shown that brazilin contains four hydroxyl groups. He has obtained the tetramethoxy-compound, and finds it has the same melting point as the trimethoxy-compound.

Tetramethylbrazilin, $C_{15}H_{10}O(OMe)_4$, is obtained by heating the trimethoxy-compound with sodium and benzene at 120°, and then, after separating the excess of sodium, heating the product with methylic iodide at 120°. It may also be obtained by heating the trimethoxy-compound with methylic iodide and potassium hydroxide. It crystallises in white leaflets, does not decompose at 110—120°, and, when melted and suddenly cooled, is converted into an amorphous modification, which melts at 66—69°. It scarcely reddens when warmed with dilute nitric acid, and dissolves in concentrated sulphuric acid, from which solution it is not precipitated by the addition of water.

When the trimethylbrazilin is treated with ethylic iodide, it yields *methyltriethylbrazilin*, $OMe \cdot C_{16}H_{10}O(OEt)_3$, which crystallises in white needles, and melts at 149°.

Trimethylbrazilin, $C_{16}H_{11}O_5Me_3$, obtained as already described by the author, is very similar to the tetramethyl compound. The *acetyl*

derivative, $C_{16}H_{10}O(OMe)_3 \cdot OAc$, melts at 172—173°, and is easily hydrolysed by alcoholic potash.

Dimethylbrazilin, $C_{16}H_{12}O_5Me_2$, sinters at 75—80°, melts at 90—91°, and, when heated with methylic iodide and sodium ethoxide, is converted into trimethylbrazilin. When treated with acetic anhydride and sodium acetate, it yields a diacetyl derivative.

Methylbrazilin, $C_{16}H_{13}O_5Me$, is obtained by reducing the corresponding brazilein derivative with zinc-dust (*Ber.*, **22**, 1560). It is a yellowish mass, which melts at 120°.

Tribromobrazilin yields a *trimethyl compound*, $C_{16}H_8Br_3O_2(OMe)_3$, which sinters at 100—105°, melts at 109—112°, and yields a *monacetyl compound*, melting at 179—180°.

Dibromobrazilin easily yields a *monacetyl* and a *diacetyl derivative;* the former melts at 170° and the latter at 249°.

When brazilin is heated with concentrated hydrochloric acid at 150°, it yields black compounds, soluble in alkalis; at 200°, it yields similar compounds, insoluble in alkalis. When heated with a large quantity of hydriodic acid and amorphous phosphorus at 200°, it yields an oil, which, on fractionation, furnishes hydrocarbons of the formulæ C_9H_{16}, b. p. 155—165°; $C_{10}H_{18}$, b. p. 170—175°; and $C_{11}H_{20}$, b. p. 180—185°. These hydrocarbons are colourless, or pale yellow, limpid liquids, and have a terpene-like odour.   E. C. R.

A Colouring Matter in Vine Leaves. By E. SCHUNCK, E. KNECHT, and L. MARCHLEWSKI (*Ber.*, **27**, 487—488).—Brown vine leaves, gathered in the autumn, were found to contain, besides 2 per cent. of potassium hydrogen tartrate, a *glucoside*, which was obtained as a brownish-yellow substance, showing some semblance of crystalline structure. When boiled with dilute sulphuric acid, this glucoside yields sugar, and a *colouring matter* which was obtained as a reddish-brown powder, and dyes chrome- and tin-mordanted wool respectively brown and yellow.   C. F. B,

Glucase. By G. H. MORRIS (*Trans. Inst. Brew.*, **6**, 132—142).— The author confirms Géduld's observation, that glucase which occurs in maize slowly hydrolyses dextrin, or perhaps, more correctly, the malto-dextrins to glucose. The author has examined the action of the cold water extracts of both germinated and ungerminated maize, barley, rye, oats, and wheat on maltose, but failed to detect the production of glucose, except in the case of maize. The reason that Lintner and Jalowetz were able to detect glucose in the product of the action on maltose of the cold-water extract of other cereals and of germinated grain, is that glucose pre-exists, ready formed in them. The author concludes that glucase is an enzyme peculiar to maize, or possibly common also to other unexamined cereals, but he does not believe that it is a normal constituent of barley or barley malt. It appears to him extremely doubtful whether it plays any part in the metabolism of the plant, or in the translocation of the carbohydrate material of this grain.   A. R. L.

Conversion of Pyrroline into Indole. By M. DENNSTEDT and F. VOIGTLÄNDER (*Ber.*, **27**, 476—480).—Pyrroline is converted into tripyrroline by dissolving 25 c.c. in 100 c.c. of 20 per cent. hydro- .chloric acid, diluting with 500 c.c. of cold water, adding dilute ammonia, little by little, until no more precipitate forms, filtering, and shaking out the filtrate twice with ether. The ethereal extract, when evaporated, leaves a residue of tripyrroline, which at once crystallises. It is well to work as rapidly as possible. Tripyrroline, on keeping, is transformed into a higher polymeride, which is insoluble in ether, and melts at 121°. When tripyrroline is heated on the water bath, it loses 1 mol. of ammonia, and leaves a transparent brown residue, which, when heated to above 300°, breaks up into indole and pyrroline, the latter of which distils over first.

C. F. B.

Synthesis of Quinoline Derivatives. By S. NIEMENTOWSKI (*Chem. Centr.*, 1893, ii, 939; from *Anzeig. Akad. Wiss. Krakau*, 1893, 244). By the condensation of anthranilic acid with acetophenone, the author obtained phenylhydroxyquinoline [Ph : OH = 2′ : 4′] (Abstr., 1886, 812). By the condensation of metahomoanthranilic -acid with acetophenone, α-phenyl-γ-hydroxymetatoluquinoline is formed. By the action of ethylic acetoacetate on anthranilic acid, γ-hydroxyquinaldine-β-carboxylic acid (Conrad and Limpach, Abstr., 1888, 1110) is produced, together with a compound, $C_{22}H_{16}N_2O_5$, which appears to be an anhydride of the former, and melts at 335°. From metahomoanthranilic acid and ethylic acetoacetate a compound, $C_{24}H_{20}N_2O_5$, melting at 350°, is obtained. This, when treated with alkalis, takes up water, forming the substance $C_{12}H_{11}NO_3$, which melts at 248°, and is probably γ-*hydroxy-α-methylmetatoluquinoline-β-carboxylic acid.* Ethylic ethylacetoacetate yields, with anthranilic acid, a compound, $C_{26}H_{24}N_2O_5$, melting at 286°, and with metahomo-anthranilic acid, a compound, $C_{28}H_{28}N_2O_5$, melting at 345°.

L. T. T.

Hydrogen Copper Quinolinate. By I. BOESEKEN (*Rec. Trav. Chim.*, 12, 253—254).—When normal copper quinolinate is boiled with nitric acid (sp. gr. 1·2), the salt, $C_{14}N_2H_8O_8Cu + H_2O$, is obtained. It crystallises from nitric acid in bunches of blue needles, blackens at 258°, and cannot be dehydrated by heating without undergoing de-composition. One part of the salt dissolves in 4320 parts of water at 15°; the salt may perhaps serve for the detection of quinolinic acid.

A. R. L.

1-Phenylpyrazolone. By F. STOLZ (*Ber.*, **27**, 407—409).—Two distinct phenylpyrazolones are known, 1-phenyl-5-pyrazolone, melting at 118°, and 1-phenyl-3-pyrazolone, melting at 153°. Now, v. Rothen-burg (*Ber.*, **26**, 2974) describes a 1-phenyl-5-pyrazolone, melting at 154—155°. Some error must have been made here, since 1-phenyl-5-pyrazolone does not melt at 154—155°, but at 118°, and the reactions obtained by v. Rothenburg with his compound, melting at 154—155°, are not given by 1-phenyl-3-pyrazolone, which would appear from the melting point to have actually been the substance

obtained by him. It is not impossible that the confusion may have arisen from the formation of a mixture of the two pyrazolones.

<div align="right">A. H.</div>

Ethylic Succinosuccinate and Hydrazine. By R. v. ROTHEN-BURG (*Ber.*, **27**, 471—473).—When ethylic succinosuccinate (1 mol.) and hydrazine acetate or hydrate (2 mols.) are boiled together in alcoholic solution, they condense into *hexahydrobenzo-3 : 4-dipyrazolone*,

$$NH<\begin{matrix}N \underline{} C - CH_2 \cdot CH \cdot CO\\ CO \cdot CH \cdot CH_2 \cdot C \underline{} N\end{matrix}>NH,$$ which crystallises in yellow prisms,

and melts at 256—257°. When heated with benzaldehyde, it yields *hexahydrobenzo-4-benzal* 3 : 4-*dipyrazolone*,

$$NH<\begin{matrix}N \underline{} C - CH_2 - C \cdot CO\\ | \diagup CHPh \diagup |\\ CO \cdot C - CH_2 - C \underline{} N\end{matrix}>NH,$$
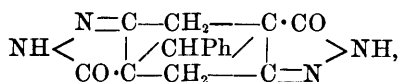
a reddish-yellow powder, which is not melted at 280°. When heated with methylic iodide at 100°, it yields 1-*dimethylhexahydrobenzo-3 : 4-dipyrazolone*, $NMe<\begin{matrix}N \underline{} C - CH_2 \cdot CH \cdot CO\\ CO \cdot CH \cdot CH_2 \cdot C \underline{} N\end{matrix}>NMe$, a yellowish powder melting above 250°; the corresponding ethyl derivative was also prepared, but was not obtained pure. When boiled with acetic anhydride, it yields 1-*diacetylhexahydrobenzo-3 : 4-dipyrazolone*, melting above 250°.

<div align="right">C. F. B.</div>

Conversion of Citrazinamide into Phenylpyrazolonecarboxylic acid. By S. RUHEMANN and F. E. ALLHUSEN (*Ber.*, **27**, 579—581).—The preparation of diketodihydroxyisonicotinamide,

$$N<\begin{matrix}CO \text{———} CO\\ C(OH){:}C(OH)\end{matrix}>C \cdot CO \cdot NH_2,$$
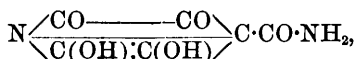
has been previously described (Abstr., 1888, 728). Attempts to obtain the corresponding acid were unsuccessful. On treatment with alkali, the compound is converted into ammonia, oxalic acid, and acetic acid. *Chlorocitrazinamide phenylhydrazone*,

$$N<\begin{matrix}CO \cdot C(N \cdot NHPh)\\ C(OH) \underline{} CCl\end{matrix}>C \cdot CO \cdot NH_2,$$
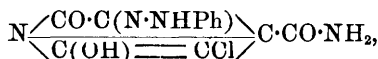
is prepared by the action of phenylhydrazine on trichlorocitrazinamide, and crystallises in lustrous, yellowish-red plates. On heating with hydrochloric acid, it is hydrolysed with production of hydrogen chloride, oxalic acid, ammonia, and phenylpyrazolonecarboxylic acid, $NPh<\begin{matrix}CO \cdot CH_2\\ N - C \cdot COOH\end{matrix}$, the formation of the latter being preceded by that of the intermediate compound,

$$NHPh \cdot N{:}C(COOH) \cdot CH_2 \cdot CO \cdot NH_2.$$

This phenylpyrazolonecarboxylic acid is isomeric with the one previously described (Trans., 1892, 799), and identical with the acid obtained by Wislicenus from ethylic oxalacetate and phenylhydrazine. The *silver salt* is gelatinous, and becomes granular on heating.

Chlorocitrazinamide phenylhydrazone dissolves in alkalis at ordinary temperatures with a dark red colour, and is precipitated unchanged on acidifying. By boiling with concentrated potash, ammonia is evolved, and *phenylhydrazoneoxalhydroxyfumaric* (*maleic*) *acid*, $COOH \cdot C(N_2HPh) \cdot C(COOH):C(OH) \cdot COOH$, is formed. The *dihydrogen potassium salt* is deposited in yellow crystals; it is unstable, and in aqueous solution readily decomposes into hydrogen potassium oxalate and 1-phenyl-5-pyrazolone-3-carboxylic acid.   J. B. T.

Action of Aromatic Aldehydes on Parasubstituted Anilines.

By O. KÜHLING (*Ber.*, **27**, 567—572).—Paranitraniline condenses with benzaldehyde in alcoholic solution in the presence of hydrochloric acid, in the proportion of 2 mols. of the former to 3 of the latter, to form derivatives of dihydroimidazole. Parachloraniline and paramidophenol give similar products, but only in very small quantity, whilst substances such as paraphenylenediamine and its dimethyl derivative do not react, or are converted into resins.

Dinitropentaphenyldihydroimidazole, $CHPh \Big\langle \begin{smallmatrix} N(C_6H_4 \cdot NO_2) \cdot CPh \\ N(C_6H_4 \cdot NO_2) \cdot CPh \end{smallmatrix}$, is obtained from benzaldehyde and paranitraniline, and forms yellowish-white needles melting at 182—183°. It is insoluble in water, sparingly soluble in alcohol, and dissolves in hot hydrochloric acid, but separates on cooling, without change. It is not altered, even on boiling, by strong concentrated aqueous potash. When treated with tin and dilute hydrochloric acid, it is converted into the corresponding *amido-compound*, which forms long, yellowish needles, containing water of crystallisation. It is insoluble in water, readily soluble in alcohol, &c., and is not altered by alkalis. The anhydrous substance melts at 122—123°. The *hydrochloride* forms soft pointed needles.

Pentanitropentaphenyldihydroimidazole, $C_{33}H_{21}N_7O_{10}$, is prepared from paranitraniline and metanitrobenzaldehyde. It is insoluble in water, very sparingly soluble in alcohol, readily in benzene, and forms a white crystalline powder melting at 227—228°. It dissolves readily in concentrated hydrochloric acid, but is precipitated without change when the solution is diluted. An isomeric substance is obtained from paranitraniline and paranitrobenzaldehyde. It is scarcely soluble in benzene or concentrated hydrochloric acid, and is a yellowish-white, micro-crystalline powder, which does not melt below 290°.

A. H

Synthesis of α-Alkyl-β-naphthocinchonic acids: Specific Reaction for Aldehydes.

By O. DOEBNER (*Ber.*, **27**, 352—354). —The formation of an α-alkyl-β-naphthocinchonic acid always takes place when an aldehyde (more than 1 mol.) and pyruvic acid (1 mol.) are dissolved in absolute alcohol, and β-naphthylamine (1 mol.), also dissolved in absolute alcohol, is added, the mixture being then heated for three hours on the water bath. The acid separates on cooling.

As pyruvic acid undergoes a partial decomposition into acetaldehyde and carbonic anhydride, a little of the α-methyl-β-naphthocinchonic acid (m. p. 310°) is formed, when no aldehyde is present in the substance to be tested.

The test does not apply to ketones, and is especially useful in deter-
mining the presence of the aldehyde group in ethereal oils. The
sugars which are represented as aldehydes (glucose, galactose) do
not give the test.   J. W.

Rotatory Power of Coniine and its Salts. By F ZECCHINI
(*Gazzetta*, **23**, ii, 601—607).—The author finds the specific rotation
of coniine to be $[\alpha]_D = +13\cdot51°$ at 23°, a number agreeing closely
with those given by former observers. In aqueous solution, its
electrical conductivity is small, and of the same order as the con-
ductivities of dimethylamine and diethylamine. Its molecular re-
fraction at 23° was also determined for the rays D, Hα, Hβ, and Hγ.

$$M\frac{\mu_D - 1}{d} = 68\cdot31. \qquad M\frac{\mu^2_D - 1}{d(\mu^2_D + 2)} = 40\cdot72.$$

Coniine has a much smaller rotatory power in benzene, alcoholic,
or aqueous solutions than when undiluted. The acetate, hydrochloride,
and hydrobromide, are optically active in alcoholic or benzene solu-
tions, the two latter salts having the same rotatory power in alcohol;
$[\alpha]_D = +4\cdot42°$. It is, however, very doubtful whether the salts are
optically active in aqueous solutions, very small rotations being
observed.   W. J. P.

Strychnine Nitrate. By GUIGNES (*J. Pharm.*, [5], **29**, 24—26).
—The product obtained by dissolving strychnine in cold or warm
dilute nitric acid, and evaporating the solution, is invariably coloured;
if, however, the alkaloïd is suspended in hot water, and dilute nitric
acid (1 : 5) added drop by drop until the liquid is neutral and dis-
solution complete, a colourless product is obtained on evaporation.
The crystals are anhydrous. Brucine nitrate remains in the mother
liquor.   JN. W.

Isomeride of Cinchonine. By E. JUNGFLEISCH and E. LÉGER
(*Compt. rend.*, **118**,|29—32).—When the dihydrobromide of hydro-
bromocinchonine is treated with alcoholic potash, as in the process of
Comstock and Koenigs, the products are cinchoniline, cinchonifine,
apocinchonine, and a small quantity of a new isomeride which the
authors call δ-cinchonine. With free hydrobromocinchonine, the
products are the same, but the proportion of apocinchonine is some-
what higher. δ-Cinchonine is separated from cinchoniline by means of
the lower relative solubility of its hydrochloride and the greater
relative solubility of the compound of its hydrochloride with zinc
chloride.

δ-Cinchonine separates from a slightly supersaturated ethereal
solution in very long prisms, insoluble in water, but extremely solu-
ble in alcohol, benzene, chloroform, and acetone, even at the ordinary
temperature. Ether readily dissolves the base at the moment of its
liberation from its salts, but gradually deposits it in long needles,
which are only slightly soluble in the same solvent. δ-Cinchonine
melts at 150°; its specific rotatory power in alcoholic solution at 17°
is $[\alpha]_D = + 125\cdot2°$, in aqueous solution containing 2 mols. HCl, it
is $[\alpha]_D = + 176\cdot9°$, and with 4 mols. HCl, $+178\cdot2°$. Solutions of

the base and its salts become brown when exposed to air and light, yielding products much less alkaline than the base itself.

The salts of δ-cinchonine are, as a rule, very soluble, and crystallise badly, but the hydrochloride, hydrobromide, and basic oxalate are less soluble, and crystallise readily. The hydrochloride forms small, colourless, highly refractive prisms containing $1\frac{1}{2}H_2O$; the hydrobromide forms similar crystals containing $2H_2O$, and the basic oxalate forms slender, colourless needles containing $5H_2O$.   C. H. B.

Aconitine. By M. FREUND and P. BECK (*Ber.*, **27**, 433—436).— The authors state that they have made 14 carbon and hydrogen determinations of crystallised aconitine, the results of which, together with other considerations mentioned below, lead them to adopt the formula $C_{34}H_{47}NO_{11}$, instead of that ascribed to the alkaloïd by Dunstan and his pupils, namely $C_{33}H_{45}NO_{12}$.

Ehrenberg and Purfürst (*Abstr.*, 1892, 1254) regarded the substance obtained by boiling aconitine with water as a mixture of the benzoates of two bases ; the authors have obtained a homogenous compound by repeatedly crystallising this product; it melts at 202—203°, and appears to have the formula $C_{39}H_{51}NO_{12}$, being the benzoate of a base $C_{32}H_{45}NO_{10}$, derived from aconitine thus :— $C_{34}H_{47}NO_{11} + H_2O = CH_3 \cdot COOH + C_{32}H_{45}NO_{10}$. The authors have examined the salts of the last-named base, and come to the conclusion that it is identical with Dunstan's isaconitine ; its properties also render it probable that it is identical with Wright's picraconitine, and they propose to retain Wright's name, picraconitine, for this base. Attempts to prepare aconitine by acetylating picraconitine have as yet yielded negative results.

It was stated above that when aconitine is boiled with water the benzoate of picraconitine is produced ; another reaction proceeds concurrently, however, in which water is assimilated and benzoic and acetic acid formed together with a base $C_{25}H_{41}NO_9$. This base is also obtained by boiling picraconitine with alcoholic potash ; it has all the properties of aconine. Since, therefore, aconitine appears to be acetylbenzoylaconine (compare Dunstan and Carr, Trans., 1894, 290), Dunstan and Passmore's observation (Trans., 1892, 401) that apoaconine is formed by benzoylating aconine must be regarded as doubtful.
    A. R. L.

[*Note.*—Dunstan (*Ber.*, **27**, 664), in reply to Freund and Beck, points out that he and his collaborateurs have already shown (Trans., 1894, 174, 290, &c.), that aconitine, on hydrolysis, yields acetic acid and "isaconitine," and that the latter is identical with Wright's "picraconitine." He has also proved that isaconitine is benzoylaconine, and therefore not isomeric with aconitine.—EDITORS.]

Action of Halogen acids on Fibrin. By J. BROD (*Chem. Centr.*, 1893, ii, 1065 ; from (*Centr. Physiol.*, **7**, 410—411).—The swelling of fibrin produced by weak hydrochloric acid increases with its concentration up to 0·8—0·9 per cent. and then diminishes. Hydrobromic acid produces less effect, and hydriodic acid less still. The hydrochloric acid present is in three conditions : (1) in combination with the calcium of the fibrin; (2) adherent, or loosely combined

with the fibrin; and (3) free. The swelling of the fibrin is greatest when the acid is present in about equal proportion in each condition.

W. D. H.

Eserine. By A. PETIT and M. POLONOVSKY (*J. Pharm.*, [5], **29**, 55—59).—Eserine or physostygmine, $C_{15}H_{21}N_3O_2$, the active principle of the Calabar bean, crystallises from benzene in large, well-defined, flat prisms, and melts at 105—106°, and not at 69° as commonly stated; the sp. rotatory power in chloroform solution is $[\alpha]_D =$ —82°, in 98 per cent. alcoholic solution, —89°, and in benzene or toluene solution, —120°. The *benzoate*, which is quite stable, crystallises in small, hard, white prisms, and melts at 115—116°; the sp. rotatory power in 98 per cent. alcoholic solution is $[\alpha]_D = 98\cdot1°$. The *parahydroxytoluate* is very hygroscopic. The *metahydroxytoluate* resembles the benzoate, and melts at 156—157°; the sp. rotatory power in 98 per cent. alcoholic solution is $[\alpha]_D = -79\cdot6°$. The *acid citrate* forms a very hygroscopic, crystalline, white powder; the sp. rotatory power in alcoholic solution is $[\alpha]_D = -74\cdot5°$. The *normal tartrate* forms very deliquescent, microscopic crystals of the cubic system. The *methiodide*, $C_{15}H_{21}N_3O_2$,MeI, crystallises in small, pale-yellow, very deliquescent prisms, and melts with decomposition at about 100°; the sp. rotatory power in 98 per cent. alcoholic solution is $[\alpha]_D = -110°$.

JN. W.

Active Principle of Dorstenia Contrayerva. By U. MUSSI (*L'Orosi*, **16**, 259—263).—The author has examined the roots of the *Dorstenia contrayerva*, a Brazilian plant which is used as an antidote to the poison of serpents and as an antiseptic; he has extracted from it two amorphous substances which he terms *cajapin* and *contrayervine*, the reactions of which are given. The latter substance yields a white, amorphous *tartrate*. No analyses are given.

W. J. P.

Ovomucoid. By C. T. MÖRNER (*Zeit. physiol. Chem.*, **18**, 525—532).—This is the name given to a proteïd-like substance which can be obtained from white of egg, after boiling, acidifying, and filtering to separate albumin and globulin. Neumeister called it pseudo-peptone. It contains only 12·65 per cent. of nitrogen, and yields a reducing substance on boiling with dilute hydrochloric acid; on concentrating its solutions slowly, they become gummy.

W. D. H.

Atmid-albumoses. By R. H. CHITTENDEN and F. S. MEARA (*J. Physiol.*, **15**, 501—534; compare Neumeister, Abstr., 1889, 910). —The experiments show that the action of superheated water on coagulated egg-albumin is essentially a hydration process, and is accompanied by cleavages of much the same order as those met with in ordinary proteolytic digestion, giving rise, on the one hand, to a resistant substance of the anti-group, only a part of which passes into albumoses by repeated cleavage of the molecule, and, on the other hand, to a more readily hydrated main-group which passes through primary and secondary albumoses into peptone, which, in turn, is broken down into leucine and tyrosine.

W. D. H.

Organic Chemistry.

Action of Nitric Acid on Saturated Hydrocarbons. By M. KONOVALOFF (*J. Russ. Chem. Soc.*, **25**, 472—500; compare this vol., i, 159).—Normal hexane was subjected to the action of nitric acid under the same conditions as were employed by the author in his previous research on the nitration of nononaphthene. Nitric acid of sp. gr. 1·155 nitrates hexane at 115—120°, but the yield of mononitrohexane is bad; acid of sp. gr. 1·075 gives a yield equal to 60 per cent. of the theoretical if the temperature is raised to 140°, the *nitrohexane* formed in this way being nearly pure. It is a colourless liquid, which boils at 176° (corr.), under a pressure of 758 mm., and has the sp. gr. 0·9509 at 0°/0°, or 0·9357 at 20°/0°. Its molecular refraction (Lorentz) is 35·26, and its odour resembles that of aniseed. When boiled with strong soda, it dissolves, and on reduction with zinc-dust and acetic acid, it gives methyl butyl ketone and normal β-hexylamine. Bromine attacks it with formation of *bromonitrohexane*, $C_6H_{12}BrNO_2$, which is a heavy, colourless liquid, volatile in a current of steam; the density is 1·3616 at 20°/0°, and the molecular refraction 42·84 From the behaviour indicated above, it would appear that the nitrohexane formed by the direct nitration of normal hexane is *methylbutylnitromethane*.

Similarly a secondary mononitro derivative, *methylamylnitromethane*, is obtained by nitrating normal heptane with nitric acid of sp. gr. 1·075 at 125—130°. It boils at 194—196°, and has the density 0·9306 at 20°/0°. The corresponding *amine* boils at 141·5° under a pressure of 761 mm., and its sp. gr. is 0·7655 at 20°/0°.

By treating normal octane with nitric acid of sp. gr. 1·075 at 130°, the author obtained a fair yield of *methylhexylnitromethane*, distilling at 210—212° under atmospheric pressure, and at 123—124° under 40 mm. pressure. The sp gr. of this nitro product was found to be 0·9201 at 20°/0°, and its molecular refraction 44·56. The corresponding *amine* boils at 163—164° under 754 mm. pressure, and its sp. gr. = 0·7745 at 20°/0°.　　　　J. W.

Suberone. By V. MARKOVNIKOFF (*J. Russ. Chem. Soc.*, **25**, 547—564).—Suberylic iodide and dilute hydrochloric acid were poured on to zinc which had been previously treated with a solution of copper sulphate. From time to time, concentrated hydrochloric acid was added, until the reduction of the iodide was complete. To purify the hydrocarbon thus obtained, it was distilled in a current of steam, treated with bromine to remove unsaturated hydrocarbons, and again distilled in a current of steam until the residue was heavier than water. The purified *suberene* (or heptamethylene, "suberane") boils at 117—117·5° under 743 mm. pressure, and its sp. gr. = 0·8094 at 20°/20°.

When allowed to remain for several days in a sealed tube with bromine and aluminium bromide, suberene is first converted into the

isomeric heptanaphthene, and then into pentabromotoluene. Hydriodic acid, in quantity insufficient for reduction, also effects the isomeric transformation into heptanaphthene at 250°.

Suberylene, C_7H_{12}, is obtained when a mixture of equal volumes of suberylic iodide and alcohol is added to strong alcoholic potash. It boils at 114·5—115° (corr.), and its sp. gr. = 0 8245 at 20°/20°.

Suberone easily dissolves in nitric acid of sp. gr. 1·30, but there is no action until the solution is warmed. The only crystalline oxidation product obtained was normal pimelic acid.   J. W.

Sulphur Compounds in Ohio Petroleum. By C. F. MABERY and A. W. SMITH (*Amer. Chem. J.*, **16**, 83—89).—In this communication the authors defend the work described in their former paper (Abstr., 1890, 350) against the criticism of Kast and Lagai (*Dingl. polyt. J.*, **284**, 69), and express their belief that the petroleums examined by the latter were probablyl not Ohio oils.   L. T. T.

Examination of Canadian Sulphur-petroleum. By C. F MABERY (*Amer. Chem. J.*, **16**, 89—93).—The crude petroleum examined had a sp. gr. of 0·86 at 20°, was rather thicker than Ohio crude petroleum, and had a slight odour of hydrogen sulphide. It contained 0·98 per cent. sulphur, and, when distilled under 250 mm. pressure, yielded 11 per cent. under 150°, containing 0 5 per cent. of sulphur; 24 per cent. between 150° and 300° (or burning oil), containing 0·64 per cent. of sulphur ; and 65 per cent. of residue above 300° containing 0·98 per cent. of sulphur. Small quantities of hydrogen sulphide were evolved during the distillation.

A preliminary examination of the sulphur oils—obtained by decomposing some of the " sludge acid " obtained in refining the burning oil distillate—showed the presence of unsaturated hydrocarbons, more or less sulphuretted, the sulphur contained in the steam-distilled product, varying from 0·43 per cent. in the fraction 32—40° to 13·93 in the fraction 160—170°. The lower fractions (principally containing the unsaturated hydrocarbons) showed a great tendency to polymerise. The original sludge sulphur-oil had a sp. gr. of 0·86, and contained 9·94 per cent. of sulphur. The author is continuing his investigations on larger quantities of this oil.   L. T. T.

Isomerism in the Cyanogen Series. By I. KONDAKOFF (*J. Russ. Chem. Soc.*, **25**, 456—466).—The author considers that most of the cyanogen compounds are of the type X·C:N, and that these enter more readily into actions involving direct addition than into double decompositions. The formation of compounds of the type X·N:C, he explains in accordance with this view by assuming that there is first direct addition between a molecule X·C:N, and a molecule of the reagent, after which there is a decomposition, with formation of a substance belonging to the type X·N:C or X·N:C:X. Thus he represents the action of silver nitrate or cyanamide as follows :
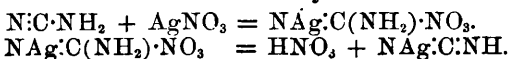
$$N:C·NH_2 + AgNO_3 = NÁg:C(NH_2)·NO_3.$$
$$NAg:C(NH_2)·NO_3 = HNO_3 + NAg:C:NH.$$
          J. W.

Crystalline Form of Potassium Isocyanate. By R. OTTO (*Ber.*, **27**, 837—838).—This salt crystallises in broad tablets, or small pyramidal crystals with a vitreous lustre. These are formed by the combination of a pyramid (111) with the plane (001), and the tablets are developed parallel to the last of these. The crystals belong to the quadratic system, and have the following constants. Axial ratio, $a : b : c = 1 : 1 : 0.5766$. Angles, (111) : ($\bar{1}_11$), 78° 22'; (111) : ($1\bar{1}1$), 53° 8'. The double refraction is very well marked and positive. No cleavage was observed.

From these measurements, it appears that the salt is isomorphous with thallium thiocyanate.　　　　　　　　　　　　　　　　A. H.

Derivatives of Acetonitrile. By W. ESCHWEILER. (*Annalen*, **278**, 229—239).—*Imidoacetonitrile*, $NH(CH_2 \cdot CN)_2$, is formed when an aqueous solution of hexamethylenamine is mixed with hydrogen cyanide (6 mols.), preferably in presence of 2 per cent. of hydrochloric or sulphuric acid; it crystallises from ether in colourless plates, melts at 75°, and decomposes above its melting point, giving rise to the odour of hydrogen cyanide and pyridine. If boiled with silver nitrate, silver cyanide is precipitated; Urech (*Ber.*, **6**, 1116) has observed the same reaction with its homologue. The *hydrochloride* crystallises in delicate needles. When imidoacetonitrile is boiled with barium hydroxide solution, diglycollamidic acid is obtained; this melts with decomposition at 225°; a small quantity of glycocine is also produced.

Nitriloacetonitrile, $N(CH_2 \cdot CN)_3$, is obtained when hexamethylenamine (100 grams) in water (500 c.c.) is mixed with 40 per cent. hydrogen cyanide (120 grams), and 35 per cent. hydrochloric acid (450 c.c.). It crystallises from water or alcohol in prisms or long needles respectively, melts at 126°, and yields triglycollamidic acid when boiled with barium hydroxide; if, however, it is heated in a sealed tube with hydrochloric acid at 150°, diglycollamidic acid is formed; in both cases a small amount of glycocine is produced.

Amidoacetonitrile is obtained, together with glycocine, by the action of ammonia on methylenecyanhydrin; when a large excess of ammonia is made use of, glycocine in almost theoretical yield is formed, whilst by the use of a very small quantity of ammonia, imidoacetonitrile and nitriloacetonitrile are the products. The last-named compound is readily prepared by adding rather more than 1 molecular proportion of fuming hydrochloric acid to a 35—40 per cent. solution of formaldehyde, and slowly dripping into the mixture a concentrated solution of potassium cyanide (1 mol.). Glycocine may be prepared by mixing equivalent quantities of potassium cyanide and ammonium sulphate, adding the calculated quantity of formaldehyde, and hydrolysing after some hours. The yield does not exceed 20 per cent. of the theoretical.　　　　　　　　　　　　A. R. L.

Amidophosphoric acid. By H. N. STOKES (*Amer. Chem. J.*, **16**, 154—155).—When ethylic chlorophosphate was treated with dry ammonia at 0° until no further increase in weight occurred, the gain in weight was 17·2 per cent., and about 20 per cent. of monamido-

phosphoric acid was isolated from the product. The reaction $POCl(OEt)_2 + 2NH_3 = NH_2 \cdot PO(OEt)_2 + NH_4Cl$, requires 19·8 per cent. increase, that of $2POCl(OEt_2) + 3NH_3 = NH[PO(OEt)_2]_2 + 2NH_4Cl$ 14·8 per cent. The observed reaction therefore took place according to both equations. When the action was carried on at 100°, ethylic chloride was evolved in large quantities, a loss of 15·8 per cent. was observed and a solid residue dissolving slowly in water was left. The action is probably expressed by the equation, $POCl(OEt)_2 + 2NH_3 = NH_2 \cdot PO(ONH_4) \cdot OEt + EtCl$, requiring a loss of 17·7 per cent. L. T. T.

Multirotation of Sugars. By P. T. MULLER (*Compt. rend.*, **118**, 425—428).—The law that governs the well-know variation in the rotatory power of sugar solutions can be ascertained on the assumption that the solution contains only two modifications of the sugar, each with its own specific rotatory power. If x represents the mass and $a\rho$ the rotatory power of the unstable modification A, and y represents the mass and ρ the rotatory power of the stable modification B, p the number of grams of dissolved matter, V the volume in cubic centimetres, l the length of the column in decimetres, and α the angle of rotation at the end of the time θ, then

$$\alpha = [(a - 1)x + p]\frac{\rho l}{V},$$

and if the final angle α_n is introduced, it can be shown that

$$\alpha = \alpha_n\left[1 + \frac{(a - 1)x}{p}\right] \text{ or } \frac{(a - 1)x}{p} = \frac{\alpha}{\alpha_n} - 1,$$

which gives the quantity of the unstable modification x transformed in the time θ. Assuming that the quantity dx transformed in the time $d\theta$ is proportional to the mass of x present

$$dx = -C'x d\theta,$$

where C' is a constant positive factor, and by integration, x_0 being the quantity transformed in time θ_0 (corresponding with a rotation α_0) it follows that

$$C = \frac{1}{\theta - \theta_0}\log\frac{\alpha_0 - \alpha_n}{\alpha - \alpha_n}.$$

By means of the results of Parcus and Tollens, the author has calculated the values of C and $\frac{\alpha_o}{\alpha_n}$ for the following sugars :—

	C.	$\frac{\alpha_0}{\alpha_n}$.
Arabinose	0·0297	1·7585
Xylose	0·0201	4·77
Rhamnose	0·0393	—
Fucose	0·0202	1·742
Galactose	0·00950	1·531
Lactose	0·00409	1·608
Maltose	0·00553	0·362

In the case of glucose, the data are at present insufficient.

C. H. B.

Formation of Mannitol in Wines. By H. MALBOT and A. MALBOT (*Bull. Soc. Chim.*, [3], **11**, 87—89).—An historical introduction. The paper is to be continued.

Action of Bases on Glucoses. By L. JESSER (*Chem. Centr.*, 1894, i, 20—22; from *Österr-ung Zeit. Zucker-Ind. Landw.*, **22**, 661—667; compare this vol., i, 4).—Baryta acts on invert sugar like calcium oxide; the acidity of the acids obtained from 2 mols. of the sugar is equivalent to $1\frac{1}{2}$ mol. of baryta, and they liberate carbonic anhydride from alkaline carbonates. The quantity of carbonic anhydride evolved on heating calcium hydroxide with levulose and invert sugar stands in molecular relationship to the amount of the levulose; practically none is evolved from the glucose (dextrose). The decomposition products of invert sugar, on titration in acid solution, exert no action on indicators, but on boiling with alkalis and acidifying, acids are liberated which affect phenolphthaleïn considerably, litmus less, and corralin scarcely at all. These acids are neutralised by boiling with acids, and in their general relationship they show a striking similarity to γ-lactones.　　J. B. T.

Action of Baryta on Glucose and Levulose. By M. H. COURTONNE (*Bied. Centr.*, **23**, 210; from *Sucrérsie indig. et colon.*, **41**, 156).—A neutral, colourless solution of invert sugar (17 grams in 100 c.c.) when slowly heated with an equivalent amount of baryta or strontia to the boiling point, gives an abundant, slightly coloured precipitate at 70° which disappears in a few minutes, yielding a strongly coloured solution which is not precipitated by carbonic anhydride, or reduced by copper solution. When twice or three times the amount of the bases are employed, the precipitate becomes brown and is only partly dissolved. In both cases, the invert sugar is completely destroyed.

The different results obtained by Beaudet, who found that glucose and levulose are not precipitated either by hot or by cold baryta, and by Beaufret, who found that glucose is partly precipitated and partly destroyed, were probably due to the strength of the solutions not having been taken into account.　　N. H. M.

Compounds of Sugars with Mercaptans. By E. FISCHER (*Ber.*, **27**, 673—679).—The author has obtained a number of compounds of certain sugars with various mercaptans, which are termed mercaptals, they differ from the alcohol glucosides recently described (this vol., i, 3) in containing two molecules of mercaptan to one of sugar. *Glucose-ethylmercaptal*, $C_6H_{12}O_5(SEt)_2$, is prepared by the addition of ethyl mercaptan to glucose dissolved in well-cooled hydrochloric acid (sp. gr. 1·19). The compound crystallises from water or absolute alcohol in slender, colourless needles, or thin plates, melts at 127—128° (uncorr.), and the refractive power $[\alpha]_D = -29\cdot8$ at 50°. It undergoes considerable decomposition on distillation, the product having the odour of roasted onions. The mercaptal has a bitter taste, it does not react with phenylhydrazine, or alkaline copper solution, and is hydrolysed by dilute mineral acids, mercuric chloride, or

silver nitrate; it dissolves in alkalis and is reprecipitated unchanged on acidifying, bromine or nitrous acid cause its decomposition; on oxidation with potassium permanganate, an acid derivative of glucose is formed which contains sulphur. With concentrated hydrochloric acid, the mercaptal becomes red and gradually changes to an oily liquid which contains sulphur, is readily soluble in water, and does not reduce alkaline copper solution. The mercaptal is without physiological action. Hydrobromic acid (sp. gr. 1·49), nitric acid (sp. gr. 1·16), sulphuric acid (50 per cent.), zinc chloride solution (50 per cent.), or even dilute hydrochloric acid may be employed to cause the condensation of the mercaptan and glucose. The *sodium salt*, $C_{10}H_{21}S_2O_5Na$, crystallises in slender needles. The *potassium salt* has also been obtained, but attempts to prepare a methyl derivative led to no definite results.

Galactose-ethylmercaptal, $C_6H_{12}O_5(SEt)_2$, is prepared in a similar manner to the preceding compound which it closely resembles; it crystallises in slender, colourless needles, melts at 140—142° (uncorr.), has a bitter taste and is lævogyrate. The yield is practically quantitative.

Arabinose-ethylmercaptal crystallises in colourless needles, melts at 124—126°, and is sparingly soluble in water.

Mannose-ethylmercaptal forms slender needles which soften at about 128°, and melt at 132—134°.

Rhamnose-ethylmercaptal crystallises in slender, lustrous plates or needles melting at 135—137°.

α-Glucoheptose-ethylmercaptal melts at 152—154°.

Xylose, lactose, and maltose also combine with ethylmercaptan, but the products are oily. *Glucose-amylmercaptal*, $C_6H_{12}O_5(SC_5H_{11})_2$, is prepared from commercial amyl mercaptan in a manner similar to the ethyl derivative and probably consists of two isomerides, it is almost insoluble in cold water, crystallises from alcohol in slender needles, melts at 138—142°, and is hydrolysed by warming with dilute hydrochloric acid.

The following crystalline compounds have also been prepared :— *galactose-amylmercaptal*, *arabinose-amylmercaptal*, *glucose-benzylmercaptal*, $C_6H_{12}O_5(SCH_2Ph)_2$, and *galactose-benzylmercaptal; xylose-amylmercaptal* is a viscid liquid. The author points out that these amylmercaptals could be advantageously employed for the detection and isolation of various sugars, on account of the readiness with which they are formed and of their sparing solubility.

Corresponding derivatives of thiophenol and of hydrogen sulphide could not be obtained, neither does fructose or sorbose appear to form mercaptals. J. B. T.

Maltol. By J. BRAND (*Ber.*, **27**, 806—810).—Caramel colouring malt, which has recently been introduced into the brewing and malt industry, is prepared by roasting malt which contains a large proportion of water; it differs, therefore, from ordinary colouring malt in possessing a considerably higher percentage of sugar. Beer, prepared from caramel malt, gives a violet coloration with ferric chloride; this is not due to salicylic acid, but to the presence of a com-

pound termed *maltol*, which is distinguished from salicylic acid by giving no reaction with Millon's reagent. The temperature employed in the manufacture of malt coffee is higher than that used in the preparation of caramel malt, and in this case maltol is formed in larger quantity, and can be isolated from the volatile products in the manner described in the original paper. Maltol readily sublimes, and is deposited in colourless, odourless crystals melting at 159°. It has the characteristic properties of a phenol, does not form an oxime or a phenylhydrazone, reduces silver solutions at ordinary temperatures, and alkaline copper solution on heating. Maltol is probably a condensation product of grape sugar, and has the formula

$$CH \underset{\displaystyle \diagdown C(OH){:}CH \diagup}{\overset{\displaystyle \diagup CH{:}C(OH) \diagdown}{\longleftarrow\!\!-\!O-\!\!\longrightarrow}} CH \, ;$$
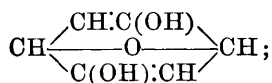
this formula most readily accounts for its properties, and agrees with the analytical results and molecular weight determination.

J. B. T.

Action of Ethylenic, Propylenic, Isobutylenic, Pseudobutylenic, and Amylenic Bromides on Trimethylamine. By G. KLEINE (*Chem. Centr.*, 1894, i, 16—18; from *Zeit. Naturw.*, **66**, 1—72). —It is known that only primary monobromo-substituted hydrocarbons form additive compounds with amines; secondary and tertiary derivatives yield unsaturated hydrocarbons and hydrogen bromide. The author finds that in the case of dibromo-hydrocarbon derivatives those alone form additive compounds with trimethylamine which contain the bromine linked to two primary carbon atoms.

The following compounds are formed by the action of isobutylenic bromide on trimethylamine: Trimethylamine hydrobromide, isocrotylic bromide, $CHBr{:}CM_2$ (b. p. 90—92°); and *isocrotyltrimethylammonium bromide*, $CMe_2{:}CH{\cdot}NMe_3Br$; this compound is homologous with neurine, which, like valeryltrimethylammonium chloride, it closely resembles in physiological action. *Dibromisobutyltrimethylammonium bromide* and *dibromisobutyltrimethylammonium dibromide* have also been prepared.

Trimethylamine and pseudobutylenic bromide in molecular proportion yield trimethylamine hydrobromide, but with 2 mols. of the base, pseudocrotylic bromide, C_4H_7Br (b. p. 90—91·8°), and hexamethylpseudobutylenediamine bromide, $C_4H_8N_2Br_2Me_6$, are also formed; the former in large, the latter in small quantity.

The following compounds are formed by the action of ethylenic bromide on trimethylamine in molecular proportion at 100° under pressure: *Tetramethylammonium bromide*, crystallising in colourless plates; trimethylamine-ethylenic bromide, $C_2H_4Br{\cdot}NMe_3Br$; trimethylamine hydrobromide in small quantity; a resinous aldehyde; hexamethylethylenediamine bromide, $C_2H_4N_2Me_6Br_2$; trimethylvinylammonium bromide (neurine bromide); dimethylamine bromide; aldehyde.

Propylenic bromide and trimethylamine at 100° yield: Trimethylamine hydrobromide; β-*propenyltrimethylammonium bromide*, $C_3H_5NMe_3Br$, a homologue of neurine; dimethylamine hydrobrom-

ide; and α-bromopropylene. Hydrogen bromide is eliminated by the action of trimethylamine (2 mols.) on propylene-bromide at the ordinary temperature.

Amylenic bromide (b. p. 74° under 15 mm. pressure) acts on trimethylamine at the ordinary temperature with formation of trimethylamine hydrobromide; at 100°, *valeryltrimethylammonium bromide*, $C_5H_9NMe_3Br$ (see above), is also produced, and combines directly with 10 atoms of bromine to form a perbromide.

<div align="right">J. B. T.</div>

β-Ethylhydroxylamine. A correction. By J. W. BRÜHL (*Ber.*, **27**, 805).—A reply to C. Kjellin (this vol., i, 223), whose claim to have independently isolated the β-alkylhydroxylamines is admitted.

<div align="right">J. B. T.</div>

Action of Hydrazine Hydrate on Ethylic Cyanacetate and Malononitrile. By R. v. ROTHENBURG (*Ber.*, **27**, 685—691).— Ethylic cyanacetoacetate readily combines with hydrazine hydrate to form *cyanacetylhydrazine*, $CN \cdot CH_2 \cdot CO \cdot NH \cdot NH_2$, which crystallises from alcohol in colourless prisms melting at 114·5—115°. It dissolves without decomposition in alkalis, alkali carbonates, and acids at ordinary temperatures; but, on heating, is hydrolysed into malonic acid, hydrazine, and ammonia. The yield of cyanacetylhydrazine is quantitative. Phenylhydrazine and hydrazine acetate do not act on ethylic cyanacetoacetate.

Cyanacetylbenzalhydrazine, $CN \cdot CH_2 \cdot CO \cdot NH \cdot N{:}CHPh$, is obtained from the preceding compound by treatment with benzaldehyde, and crystallises from alcohol in colourless plates melting at 174·5°; by acids or alkalis, it is resolved into its constituents.

Cyanacetylisopropylhydrazine, $CN \cdot CH_2 \cdot CO \cdot NH \cdot N{:}CMe_2$, formed from cyanacetylhydrazine and acetone, resembles the benzal derivative; it crystallises in large, colourless, flat needles, and melts at 152°.

Cyanacetylorthohydroxybenzalhydrazine,

$$CN \cdot CH_2 \cdot CO \cdot NH \cdot N{:}CH \cdot C_6H_4 \cdot OH,$$

from cyanacetylhydrazine and salicylaldehyde, crystallises from alcohol in small, yellow needles, and melts at 169°.

Ethylic cyanacetylhydrazinepyruvate, $CN \cdot CH_2 \cdot CO \cdot NH \cdot N{:}CMe \cdot COOEt$, is obtained by the action of ethylic pyruvate on the hydrazine; it is crystalline, and melts at 144°.

Ethylic cyanacetylhydrazineacetoacetate,

$$CN \cdot CH_2 \cdot CO \cdot NH \cdot N{:}CMe \cdot CH_2 \cdot COOEt,$$

is prepared in a manner similar to the preceding compound, and crystallises in needles melting at 98°.

Cyanacetylacetylhydrazine, $CN \cdot CH_2 \cdot CO \cdot NH \cdot NHAc$, formed from acetic anhydride and the hydrazine, crystallises from alcohol, and melts at 172°.

Cyanacetylbenzenesulphonylhydrazine, $CN \cdot CH_2 \cdot CO \cdot NH \cdot NH \cdot SO_2Ph$, is formed by the action of benzenesulphonic chloride and soda on the hydrazine; it is crystalline, and melts at 176°.

Attempts to convert cyanacetylhydrazine or its compounds into pyrazolidone- or pyrazolone-derivatives were unsuccessful.

Symmetrical dicyanacetylhydrazine, $N_2H_2(CO \cdot CH_2 \cdot CN)_2$, is prepared by the action of iodine on cyanacetylhydrazine, or by heating the ethylic acetoacetate-derivative at $100°$; it forms granular crystals, and melts at $162°$. A red, crystalline compound, which melts at $156°$, and is probably *formazylic cyanide*, $CN \cdot C(N \cdot NHPh) \cdot N:NPh$, is obtained by the action of diazobenzene chloride on ethylic cyanacetate in alkaline solution.

$3:5$-*Diamidopyrazole*, $NH {\Large<} {\begin{matrix} N \vdots C(NH_2) \\ C(NH_2):CH \end{matrix}} {\Large>}$, is formed by the inter-action of hydrazine hydrate or acetate, and malononitrile at ordinary temperatures; it is a dark brown, oily liquid, and has not yet been purified; with ferric chloride, a violet dye is produced, which is sparingly soluble. The *picrate* crystallises in reddish plates, darkens at $230—240°$, and decomposes at $250°$.

$3:5$-*Dibenzaldiamidopyrazole*, $NH {\Large<} {\begin{matrix} N \vdots C(N:CHPh) \\ C(N:CHPh):CH \end{matrix}} {\Large>}$, is prepared by the action of benzaldehyde on the pyrazole; it crystallises with difficulty, and melts at about $170°$.

Hydrazine picrate, $N_2H_4,C_6H_3N_3O_7$, is an extremely characteristic derivative of hydrazine; it crystallises from alcohol in pale yellow needles, melts at $184°$, does not explode when heated on platinum foil, and is more sparingly soluble than phenylhydrazine picrate.

J. B. T.

The "Dinitroalkylic acids." By A. P. N. FRANCHIMONT and H. VAN ERP (*Rec. Trav. Chim.*, **12**, 330—333).—Dilute sulphuric acid seems to have no action on the zinc or copper derivative of methyl-nitramine, other than liberating the amine. On treating Frankland's zinc or copper "dinitromethylate" in a similar manner, gas is evolved in small quantities, and a substance of higher melting point than methylnitramine is obtained. The authors are investigating these compounds.

W. J. P.

Complex Metallic Bases. By N. KURNAKOFF (*J. Russ. Chem. Soc.*, **25**, 565—618).—When an aqueous solution of potassium chloroplatinite is added in excess to a solution of thiocarbamide at the ordinary temperature, the compounds $PtCl_2,2CS(NH_2)_2$ and $PtCl_2,CS(NH_2)_2$ are precipitated, and on warming these with excess of thiocarbamide they are transformed into the soluble compound $PtCl_2,4CS(NH_2)_2$, which is of the character of Reiset's first base. When a warm, concentrated solution of potassium chloroplatinite is poured into a warm, saturated solution of thiocarbamide, there is considerable development of heat, and the liquid, on cooling, deposits fine needles of the salt $PtCl_2,4CS(NH_2)_2$. Hydrogen sulphide does not precipitate a solution of this salt, but the alkalis give amorphous orange precipitates. The compound is easily oxidized, the sulphur being converted into sulphuric acid. The corresponding bromide, sulphate, nitrate, chloroplatinate, and chloroplatinite were prepared from it.

The salt, $PtCl_2,2CS(NH_2)_2$, unites with pyridine, forming the compound $PtCl_2,2CS(NH_2)_2,2C_5H_5N$.

The palladium compound, $PdCl_2,4CS(NH_2)_2$, was obtained in an analogous manner to the corresponding platinum compound.

Substituted thiocarbamides give similar salts with 2 and 4 mols. of base to 1 mol. of platinous chloride. Mixed salts containing thiocarbamides and pyridine or ammonia can easily be prepared, various isomerides existing.

Thioacetamide forms analogous platinum bases, which are, however, less stable than the thiocarbamide bases, especially in presence of water. Xanthogenamide bases were also prepared.

The author discusses at considerable length the constitution of the compounds obtained by him.　　　　　　　　　　　　　J. W.

Aliphatic Acids of Lanolin. By J. DE SANCTIS (*Gazzetta*, **24,** i, 14—28).—Lanolin was treated with hot sodium ethoxide solution, and the sodium salts deposited were then extracted with ether to remove basic compounds. The acids not volatile in a current of steam were found to be cerotic, palmitic, normal caproic, and oleïc acids. Those volatile in a current of steam were stearic, isovaleric, and normal butyric acids. The acids were separated by means of their lead salts, and analysed quantitatively.　　　　　W. J. P.

Constitution of Ethylic Acetoacetate. By H. V. PECHMANN (*Annalen*, **278,** 223—228).—One of the most weighty arguments advanced by Nef (Abstr., 1893, i, 629) in support of the hydroxyl formula for ethylic acetoacetate is the formation by direct acetylation of the so-called ethylic β-acetisocrotonate. The author's experiments show that only traces of the acetoxy-compound are formed by protracted boiling of ethylic acetoacetate with a large excess of acetic anhydride (compare also Claisen, this vol., i, 31). Nef (*loc. cit.*) distils off most of the acetic anhydride from the product of the action, and shakes the residual oil with soda, the undissolved portion being ethylic β-acetisocrotonate. The author contends, therefore, that proof is wanting that this acetoxy-compound is produced by direct acetylation, for he has previously shown (*Ber.*, **25,** 1046) that the same acetoxy-compound (ethylic triacetoacetate) is produced together with ethylic diacetoacetate, when ethylic acetoacetate is shaken with acetic anhydride and soda.　　　　　A. R. L.

Pyruvic acid. By R. OTTO (*Ber.*, **27,** 838).—The author has noticed the occurrence of pyruvic acid in a solution of tartaric acid which had been kept for some years exposed to light. The solution was dark yellow, and smelled of caramel.　　　　　A. H.

Formation of Hydroxamic acids from Ethereal Salts. By A. HANTZSCH (*Ber.*, **27,** 799—804).—The action of hydroxylamine on ethylic oxalacetate was investigated by the author some years ago, when a crystalline acid was obtained, from which a number of derivatives were prepared and analysed; on recently repeating the work, it was found that some unknown substance had been supplied instead of ethylic oxalacetate, and attempts to determine the nature of this substance led to the preparation of the compounds described below. Dihydroxamic acids are most conveniently obtained by dissolving the ethereal dicarboxylate in concentrated aqueous hydroxylamine solu-

tion, and adding concentrated alkali, or saturating the liquid with ammonia, the sparingly soluble ammonium or alkali salt is then decomposed by acids. Oxaldihydroxamic acid, $NOH:C\cdot C:NOH$, melts at 165°, instead of 105°, as stated by Lossen; the yield is quantitative. *Malonodihydroxamic acid*, $CH_2[C(OH):NOH]_2$, crystallises from water in large, lustrous, prisms, melting at 154—155° with violent decomposition; it is insoluble in ether, and has only a feebly acid action. The *ammonium salt*, $C_3H_9N_3O_4$, readily evolves ammonia, and melts at 141° with decomposition. The *copper salt* dissolves in excess of cupric acetate solution, but is insoluble in presence of sodium chloride, or ammonium chloride. *Ammonium malonhydroxamate*, $NOH:C(OH)\cdot CH_2\cdot COONH_4$, is prepared by prolonged boiling of the preceding ammonium salt in aqueous solution, and melts at 181°. The action of hydroxylamine on ethylic succinate and ethylic acetate is similar to its action on ethylic malonate, and will be described later. J. B. T.

Constitution of Platoso-oxalyl Compounds. By H. G. SÖDERBAUM (*Zeit. Anorg. Chem.*, **6**, 45—48).—Werner (*ibid.*, **3**, 317) seeks to account, on stereochemical grounds, for the isomerism of the platoso-oxalyl compounds, originally prepared by the author. The validity of this explanation rests on the hypothesis that these compounds contain 2 mols. of water, which cannot be eliminated without decomposing the compounds. Whilst this is true of the ammonium derivatives, it is not true of the potassium derivatives, which lose their water without decomposition and show the same isomerism when anhydrous. Some light may be thrown on the isomerism by the fact that the dark potassium platoso-oxalyl compound gives an acid derivative, $HK_5Pt_3(C_2O_4)_6 + 6H_2O$, whilst the yellow variety gives no such derivative. A. G. B.

Solubility of Metallic Oxides in Normal Potassium Salts of Tartaric and other Organic acids. By L. KAHLENBERG and H. W. HILLYER (*Amer. Chem. J.*, **16**, 94—108).—Observing that when lead oxide is added to a boiling solution of normal potassium tartrate it is freely dissolved and the solution becomes alkaline owing to liberation of potassium hydroxide, the authors have investigated the action. Lead oxide is freely dissolved until the solution contains lead oxide and potassium tartrate in molecular proportion; beyond this point, solution takes place with difficulty only, but by long-continued boiling with pretty strong solutions of the tartrate, the authors succeeded in dissolving about 1·24 mol. proportions of lead oxide in 1 mol. proportion of potassium tartrate. Where the ratio of oxide to tartrate is one or more, only half the potassium in the tartrate is liberated as hydroxide. From a strong boiling solution containing excess of lead, a precipitate is formed, on cooling, which is a basic lead tartrate of the formula $(PbO)_2C_4H_4O_6Pb$. From weaker solutions, alcohol causes a precipitate of the approximate composition Pb 56·5 per cent., K 10·6, C 9·2, H 0·9, which is probably a mixture of a tartrate of the proportion Pb : K = 1 : 1 with a more basic lead tartrate. When precipitated lead tartrate is treated with 2 mol. proportions of potash in

aqueous solution, the same potassium lead tartrate seems to be formed, as the lead tartrate is dissolved, and only half the potash remains in the free state. The normal tartrates of sodium, lithium, rubidium, and ammonium act like potassium tartrate, but thallium tartrate and potassium antimonyl tartrate do not act on lead oxide. When potassium ethylic tartrate is treated with lead oxide, it is saponified, but the resulting white lead salt goes into solution only on adding an alkali hydroxide. Hydrogen potassium tartrate acts on lead oxide like ethylic potassium tartrate, only much more slowly ; the action is much accelerated by the addition of a little potassium hydroxide. The following oxides, As_2O_3, Sb_2O_3, SnO_2. Bi_2O_3, HgO, Ag_2O, Pb_3O_4, CuO, Fe_2O_3, Al_2O_3, Cr_2O_3, MnO_2, ZnO, MgO, BeO, Er_2O_3, Ce_2O_3, Di_2O_3, and UO_3, were found to have no action on normal potassium tartrate.

Potassium malate, citrate, lactate, and glycerate take up but insignificant quantities of lead oxide, whilst potassium succinate, malonate, acetate, and propionate do not act on it. Potassium mucate and potassium saccharate act on lead oxide in a similar way to the tartrate, forming known basic salts of the probable formulæ $C_6H_4O_8Pb_3$. The reactions take place between 2 mols. of lead oxide and 1 of mucate or saccharate. From their results, the authors consider the following conclusions as probable :— 1. In order that its normal potassium salt may react readily with lead oxide, the organic acid must be bibasic, and must contain two, or a multiple of two, alcoholic hydroxyl groups. 2. The number of molecules of the oxide with which 1 mol. of salt readily reacts is equal to one-half the number of alcoholic hydroxyl groups contained in the acid.   L. T. T.

Preparation of Lead Triethide. By A. GHIRA (*Gazzetta*, **24**, i, 42—45).—Löwig and Klippel (*Gmelin's Handbook*) gave a method for preparing lead triethide by the action of ethylic iodide on an amalgam of lead and sodium. Numerous attempts to prepare the substance have, however, failed, lead tetrethide being obtained instead ; the author suggests that the difficulties met with in analysing the product are probably the cause of the error into which Löwig and Klippel fell.   W. J. P.

Sulphonation of Thiophen and its Oxidation by Sulphuric acid to a new Dithienyl. By A. TÖHL (*Ber.*, **27**, 665—667).— When thiophen (5 grams) is added to faintly fuming sulphuric acid (50 grams), well cooled with ice-cold water, and then subjected to steam distillation, a fairly good yield of a dithienyl isomeric with the compound obtained by Nahnsen, is obtained, and the remainder of the thiophen may be recovered from the acid solution as the barium or lead sulphonate.

The *dithienyl*, $C_8H_6S_2$, crystallises in large, colourless leaflets, melts at 33°, boils at 260° (uncorr.) under the ordinary pressure, without decomposition, and, with sulphuric acid, gives a yellow solution having a green fluorescence. When the solution in sulphuric acid is warmed with isatin, a beautiful bluish-violet coloration is produced.

Perbromodithienyl, $C_8Br_6S_2$, is obtained by warming dithienyl dis-

solved in acetic acid with excess of bromine. It crystallises in needles and melts at 257° (uncorr.).

Bromothiophen is also partially converted into bromodithienyl by the action of concentrated sulphuric acid, but other reactions also take place. Dibromothiophen yields a brominated dithienyl, dibromothiophensulphonic acid, sulphonic acids containing less bromine and tribromothiophen.   E. C. R.

Action of Nitric Acid on Aromatic Hydrocarbons. By M. KONOVALOFF (*J. Russ. Chem. Soc.*, **25**, 509—546).—Benzene is scarcely attacked by nitric acid of sp. gr. 1·075 at 125—130°. Toluene, under the same conditions, gives benzoic acid, but, if heated with the acid for a long time at 105°, it gives small quantities of a nitro-compound boiling at 115°. Ethylbenzene, when heated with the acid at 105—110°, gives a yield of about 63 per cent. of an oil which decomposes when distilled even under reduced pressure.

The crystalline potassium salt obtained from the crude product may be purified by recrystallisation from alcohol. When carbonic anhydride is passed into its alcoholic solution, or when the salt is treated with dilute nitric, acetic, or sulphuric acid, a mixture of acetophenone and phenylnitroethane is formed. An aqueous solution of the potassium salt, however, when decomposed by a current of hydrogen sulphide yields pure *phenylnitroethane*, $CHMePh \cdot NO_2$. This is volatile in a current of steam, and under a pressure of 25 mm. distils at 135° without undergoing any appreciable decomposition. At the atmospheric pressure, it boils at 230—236°, but there is considerable decomposition. It is a colourless liquid, which does not crystallise at —15°; its sp. gr. = 1·1202 at 20°/0°, and its molecular refractive power is 41·379. In alkalis, it dissolves readily with formation of alkali salts which may be easily obtained in the crystalline form. Salts of the heavy metals give coloured precipitates with solutions of the sodium salt. Phenylnitroethane behaves as a secondary nitro-compound with nitrous acid. It is not attacked by bromine, but its potassium salt yields a *monobromide*, $C_8H_8BrNO_2$, which is a yellow oil having a sp. gr. of 1·5182 at 20°/0°.

On reduction with zinc dust in alkaline solution, phenylnitroethane yields *α-phenylethylamine*, $CHMePh \cdot NH_2$, which boils at 186—189°. Its hydrochloride crystallises in long, flat needles, and melts at 155°.

Propylbenzene is attacked by nitric acid of sp. gr. 1·075 under the same conditions as ethylbenzene. The chief product of the action is *phenylnitropropane*, $C_9H_{11} \cdot NO_2$, which boils at 141° under 25 mm. pressure without undergoing decomposition. Its sp. gr. at 20°/0° is 1·0866. It forms soluble alkali salts whose solutions are precipitated by salts of the heavy metals. On treatment with stannous chloride in acid solution, it yields ethyl phenyl ketone and *phenylamidopropane*, $CHEtPh \cdot NH_2$; this boils at 204—206°, and its sp. gr. = 0·9424 at 20°/0°.

Pseudocumene, with nitric acid of sp. gr. 1·075 at 105—110°, gives a mixture of two *xylylnitromethanes*, namely, $C_6H_3Me_2 \cdot CH_2 \cdot NO_2$ [1 : 3 : 4] and [1 : 2 : 4].   J. W.

Derivatives of Mesitylene. Hydrolysis of Aromatic Nitriles.
By F. W. KÜSTER and A. STALLBERG (*Annalen*, **278**, 207—223).—
Preparation of Mesitylene—A cold mixture of concentrated sulphuric
acid and water (2 : 1) is gradually added to commercial acetone con-
tained in a reflux apparatus, and, after remaining 24 hours, the
mixture is slowly distilled. Unaltered acetone first passes over, and
subsequently (between 150° and 200°) crude mesitylene, which is
shaken with sodium hydroxide and purified by fractional distillation
over sodium ; the yield is 13·5 per cent. of the theoretical.

β-Isoduronitrile, $C_6H_2Me_3\cdot CN$ [Me_3 : CN $= 1 : 3 : 5 : 4$], is ob-
tained from mesidine by Sandmeyer's method together with a little
mesitol. The authors find that mesitol melts at 70—71° ; β-isoduro-
nitrile at 55°. The latter cannot be converted into the carboxylic
acid either by heating it with acids or alkalis, and it is noteworthy
that tetramethylbenzonitrile (Abstr., 1884, 1320) and pentamethyl-
benzonitrile (Abstr., 1885, 1128) are similarly indifferent. In each of
these compounds, the hydrogen atoms contiguous to the cyano-group
are replaced by methyl. The experiments to be described were made
to ascertain the behaviour of derivatives of β-isoduronitrile in which
negative radicles are substituted for the hydrogen atoms.

Nitro-β-isoduronitrile, $NO_2\cdot C_6HMe_3\cdot CN$, is obtained by nitrating
β-isoduronitrile, but, more conveniently from dinitromesitylene
(Fittig, *Annalen*, **141**, 133). The dinitromesitylene is heated with
alcoholic ammonium sulphide in an autoclave at 100° for 20 hours,
and the resulting nitramidomesitylene converted into *nitro-β-isoduro-
nitrile* by Sandmeyer's method ; this boils at 277·5° (750 mm.), and
melts at 90°. When heated with concentrated hydrochloric acid for
six hours at 180—200°, *nitro-β-isodurylic acid*, $NO_2\cdot C_6HMe_3\cdot COOH$, is
obtained ; it melts at 182°. A small quantity of *nitro-β-isoduramide*,
$NO_2\cdot C_6HMe_3\cdot CO\cdot NH_2$, is also simultaneously produced ; in one ex-
periment, the authors obtained a quantitative yield of the amide by
boiling the nitrile with dilute sulphuric acid.

Amido-β-isoduronitrile, $NH_2\cdot C_6HMe_3\cdot CN$, is obtained when the cor-
responding nitro-derivative is reduced with stannous chloride ; it
crystallises in long, delicate needles, melts at 35°, and gives the
dinitrile, $C_6HMe_3(CN)_2$, by Sandmeyer's method. The latter melts
at 142°, and cannot be hydrolysed. *Nitrodicyanomesitylene*,
$NO_2\cdot C_6Me_3(CN)_2$, is formed by warming the last compound with
fuming nitric acid ; it melts at 118°.

Dinitro-β-isoduronitrile, $CN\cdot C_6Me_3(NO)_2$, is obtained by heating the
corresponding mononitro-derivative, described above, with a mixture
of equal volumes of concentrated sulphuric acid and fuming nitric
acid ; it forms white needles, melts at 178°, and yields *dinitro-β-
isodurylic acid*, $C_6Me_3(NO_2)_2\cdot COOH$, when heated with concentrated
hydrochloric acid at 200—210° ; the latter melts at 228°, and its
amide melts at 198°. *Nitramido-β-isoduronitrile*, $NO_2\cdot C_6Me_3(NH_2)\cdot CN$,
is prepared by heating the dinitro-compound with alcoholic am-
monium sulphide in an autoclave at 100° ; it melts at 230°, and yields
nitro-dicyanomesitylene (m. p. 118° ; see above) by Sandmeyer's
method.

Amidodicyanomesitylene, $NH_2\cdot C_6Me_3(CN)_2$, is obtained by reducing

the nitro-compound with stannous chloride; it melts at 135°, and, if treated by Sandmeyer's method, yields the *tricyano*-derivative, $C_6Me_3(CN)_3$, which melts at 165°, and cannot be hydrolysed.

<div align="right">A. R. L.</div>

Orthocyanobenzylic Cyanide. By S. GABRIEL and T. POSNER (*Ber.*, **27**, 827—837).—By the action of sodium ethoxide on "diacetylorthocyanobenzylic cyanide" (Abstr., 1893, i, 228), a compound is obtained which crystallises from alcohol, melts at 119°, and on treatment with hydriodic acid, is resolved into ethylic iodide and methylcyanisocarbostyril, the compound is, therefore, *α-orthocyano-β-ethoxyallylbenzene*, $CN \cdot C_6H_4 \cdot C(CN) \colon CMe \cdot OEt$, and the formation of methylcyanisocarbostyril is preceded by that of the hypothetical compound, $CN \cdot C_6H_4 \cdot C(CN) \colon CMe \cdot OH$. The production of the allylbenzene derivative shows that "diacetylorthocyanobenzylic cyanide" has the formula $CN \cdot C_6H_4 \cdot C(CN) \colon CMe \cdot OAc$, and should accordingly be termed *ψ-diacetylcyanobenzylic cyanide*.

$1:3$-*Methoxymethylisoquinoline*, $C_6H_4 {<}{}^{\text{CH} \underline{\quad\quad} \text{CMe}}_{(\text{COMe}) \colon \text{N}}$, is prepared by the action of sodium methoxide on chloromethylisoquinoline, it melts at 32°, forming a colourless, viscid liquid, and boils at 258° under a pressure of 764 mm. With acids, it yields salts which are decomposed by water. $1:3$-*Ethoxymethylisoquinoline* is prepared in a similar manner to the methoxy-derivative which it closely resembles; it boils at 266° under 764 mm. pressure.

By the action of benzoic chloride on orthocyanbenzylic cyanide in presence of potash, *ortho-α-dicyano-β-hydroxystilbene*,

$$CN \cdot C_6H_4 \cdot C(CN) \colon CPh \cdot OH,$$

is formed, and not *benzoylcyanobenzylic cyanide*, $CN \cdot C_6H_4 \cdot CHBz \cdot CN$, as might be expected; it crystallises from ether in colourless, transparent, needles, and melts at 105—106° or 109—110°, according to the rapidity of heating; at higher temperatures (110—120°) it is converted into a yellow crystalline compound, which melts at 290°. The *silver salt* is yellow and flocculent; the *potassium salt* is crystalline, and on treatment with hydrochloric acid is converted into cyanophenylisocoumarin, which is colourless, and not lemon coloured as previously stated (*loc. cit.*); phenylcyanisocarbostyril melts at 285°.

By the action of hydrogen chloride on dicyanohydroxystilbene in ethereal solution, a pulverulent, colourless additive compound, $C_{16}H_{11}N_2OCl$ is formed, which softens at 220° and melts at about 270°; on treatment with hydrochloric acid at 100°, the compound $C_{16}H_{13}N_2O_2Cl$ is obtained in microscopic needles, melting at 196°. *Acetylortho-α-dicyano-β-hydroxystilbene*, $CN \cdot C_6H_4 \cdot C(CN) \colon CPh \cdot OAc$, crystallises in needles and melts at 211—213°. The *ethoxy derivative*, $CN \cdot C_6H_4 \cdot C(CN) \colon CPh \cdot OEt$, prepared from the silver or potassium salt, crystallises in transparent prisms, melting at 115—116°; and on treatment with hydriodic acid is resolved into ethylic iodide, ammonia, and cyanophenylisocoumarin. The *methoxy-derivative* crystallises in colourless needles, melting at 140—143°.

Ortho-α-tricyanodibenzyl, $CN \cdot C_6H_4 \cdot CH(CN) \cdot CH_2 \cdot C_6H_4 \cdot CN$, is pre-

pared by the action of alcoholic potash on a mixture of cyanobenzylic cyanide and cyanobenzylic chloride, and is formed in small quantity in the preparation of dicyanohydroxystilbene; it crystallises from alcohol, melts at 114°, and is being further investigated.

By the action of soda on orthocyanobenzylic cyanide a yellow basic compound is obtained, which is insoluble in ordinary media, but dissolves in dilute acids and in alkalis, but not in ammonia. The *hydrochloride*, $C_9H_8N_2O,HCl + H_2O$, crystallises in greenish-white, flat needles, and decomposes at 190—200°. The *picrate* is yellow and crystalline, and melts at 195—205° with decomposition.

J. B. T.

Ethylphenols. By A. BÉHAL and E. CHOAY (*Compt. rend.*, **118**, 422—425).—Three ethylphenols have been described, and the authors have investigated these compounds, using new methods of preparation. The ortho- and para- derivatives were obtained by nitrating ethylbenzene, reducing to amines, and converting the latter into acetyl-derivatives, which were separated by means of the greater solubility of the ortho-derivative in water. The ortho-compound was purified by crystallisation from alcohol, and melts at 111—112°; the para-derivative was crystallised from benzene, and melts at 92°. These amides, when boiled with hydrochloric acid, are rapidly converted into amines, and when the latter are diazotised in dilute sulphuric acid they yield the phenols in a state of purity.

In the preparation of the meta-derivative, the acetyl-derivative of parethylphenylamine was nitrated, boiled with hydrochloric acid to remove the acetyl-group, and then treated with amylic nitrite in presence of sulphuric acid and absolute alcohol to remove the amide group. The metanitroethylbenzene thus obtained was reduced with iron and acetic acid, and then diazotised in presence of dilute sulphuric acid.

Ortho-ethylphenol boils at 202—203°; sp. gr. at 0° = 1·0371. With ferric chloride, it gives a blue-violet coloration. The benzoate boils at 314°, and crystallises from alcohol in large crystals, which melt at 39°.

Meta-ethylphenol boils at 214°, and separates from methylic chloride in crystals, which melt at −4°. With ferric chloride, it gives a violet coloration. The benzoate crystallises readily from alcohol, melts at 52°, and boils at 322°; the acetate boils at 222—223°, sp. gr. at 0° = 1·0403.

Parethylphenol melts at 45—46° and boils at 215—216°; it is slightly soluble in cold water, more soluble in hot water, and very soluble in alcohol, ether, and benzene. With ferric chloride, it gives a blue coloration with a violet tinge. The benzoate boils at 328°, and crystallises from alcohol of 95° in lamellæ, which melt at 59—60°. Parethylphenol is identical with the compound hitherto distinguished as α-ethylphenol.

C. H. B.

Constitution of Orcinol. By DE FORCRAND (*Compt. rend.*, **118**, 421—422).—The thermal value of the first function of orcinol is +40·23 Cal., and of the second function 39·13 Cal., the mean value

being 39·68 Cal. The difference between the two values is smaller than in the case of the para-phenols, and much smaller than in the case of ortho-phenols. It follows that in orcinol the hydroxyl groups are in the meta position as in resorcinol. The excess of acidity seems to be due to the first function, since the thermal value of the second function is practically identical with that of ordinary phenol.

C. H. B.

Action of Aldehydes on Nitroso-derivatives. By J. Pinnow and G. Piston (*Ber.*, **27**, 602—609; compare Abstr., 1893, i, 509).— Methylic iodide forms no additive product with 1 : 4-formylamido-dimethylaniline, $CHO·NH·C_6H_4·NMe_2$; the formyl group is eliminated, and penta- or tri-methylphenylenediamine iodide formed, according to circumstances. Nitrous acid converts it into 1 : 3 : 4-*nitroformyl-amidodimethylaniline*, $CHO·NH·C_6H_3(NO_2)·NMe_2$, which crystallises in lustrous red needles melting at 86°, and can be transformed by reduction with tin and hydrochloric acid into the already known 1 : 3 : 4-dimethyltriamidobenzene, $C_6H_3(NH_2)_2·NMe_2$. This base yields an acetyl derivative when mixed with acetic anhydride; if the mixture is heated, methylic acetate is formed (showing that a methyl group has been removed) together with *methylethenylacetylamido-phenyleneamidine*, $NHAc·C_6H_3{<}^{NMe}_{N}{\geqslant}CMe + H_2O$, which crystal-

lises in plates, melts when anhydrous at 238·5°, yields a *picrate*, with $1C_6H_3N_3O_7$, melting at 226°, and, when boiled with hydrochloric acid, loses the acetyl-group, yielding the base itself, which crystallises in white plates, stable in air, and melting at 76°. Pure para-formaldehyde yields the same products with nitrosodimethylaniline as does the 40 per cent. solution of formaldehyde, only the action is more violent, and more resinous products are formed. Formaldehyde has also some reducing action on nitrosodimethylamine, in which the nitroso-group is joined to nitrogen instead of to carbon; no definite compounds could, however, be isolated from the product.

Acetaldehyde has no action on nitrosodimethylaniline. Form-aldehyde is thus the only aldehyde that is capable of reducing the nitroso- to the amido-group.

C. F. B.

Reactions of Orthotolidine. By H. Schiff and A. Ostrogovich (*Annalen*, **278**. 375—379. and *Gazzetta*, **24**, i. 56—60: compare this vol., i, 236).—*Orthotolidine hydrochloride*, $C_{14}H_{16}N_2,HCl$, is obtained by boiling the dihydrochloride with sodium acetate in aqueous solution. It crystallises in lustrous, colourless scales, which decompose at above 300°, and soon redden on exposure to the air; even in small quantities it provokes violent sneezing. It is readily soluble in hydrochloric acid yielding the dihydrochloride; the monhydro-chloride is recommended as a source for obtaining pure salts of orthotolidine. The monhydrochloride yields diacetyltolidine when heated with acetic anhydride or glacial acetic acid; with potassium cyanate, carbonic anhydride and tolidine are formed, and on treat-ment with ethylic chlorocarbonate the dihydrochloride and tolidindi-urethane melting at 190—190·5° are obtained.

The dihydrochloride is soluble in 17·34 parts of water at 12°, and the monhydrochloride in 112·4 parts. W. J. P.

Aromatic Diazo-compounds and Nitrosamines. By H. v. PECHMANN and L. FROBENIUS (*Ber.*, **27**, 651—658; compare Abstr., 1893, i, 154).—The authors have already shown that by the action of benzoic chloride on alkaline solutions of diazo-compounds a benzoylated nitrosamine is formed. Acetic anhydride acts in a similar way, and yields acetylated nitrosamines; these are identical with the compounds obtained by the action of nitrous acid on acid anilides.

Benzoylparatolylnitrosamine, $C_7H_7\cdot NBz\cdot NO$, is obtained by shaking an alkaline solution of diazotoluene containing sodium acetate with benzoic chloride. It crystallises in pale, yellow needles, explodes at 74—75°, decomposes on exposure to air or in a closed vessel, and decomposes in solution yielding benzotoluidide and nitrous acid. When reduced with zinc dust and acetic acid, it yields benzotoluidide.

Benzoylphenylnitrosamine crystallises in yellow needles and explodes at 75—76°.

Acetylparatolylnitrosamine, $C_7H_7\cdot NAc\cdot NO$, obtained from diazotoluene and acetic anhydride, melts at 80°, and has the properties assigned to it by O. Fischer, who prepared it by the action of nitrous acid on acetoluidide.

Thus aromatic amines, when treated with nitrous acid and then with acetic anhydride, or *vice versâ*, yield the same compounds; whence the authors conclude that diazobenzene and acetanilide have analogous constitutions, that is that diazobenzene is the anilide of nitrous acid. In accordance with this view is the production of nitrous acid when an alkaline solution of diazobenzene is gradually added to a boiling concentrated solution of sodium hydroxide.

When diphenylnitrosamine and paratoluidine, dissolved in light petroleum, are left for about a week, diazoamidotoluene is formed; a reaction which the authors explain by supposing that the nitrosamine loses its nitroso-group, which then diazotises the toluidine. Nitroso-anilides react easily with amido-compounds, and thus show a similarity to diazobenzene. Nitroso-acetanilide and toluidine yield diazoamidobenzenetoluene when mixed in molecular proportion; if an excess of base is present, then diazoamidotoluene is obtained. Acetylparatolynitrosamine and aniline also yield diazoamidobenzenetoluene. Nitrosoanilides also react with phenols, and acetylparatolylnitrosamine and resorcinol yield paratolueneazoresorcinol. E. C. R.

Paranitrodiazobenzene. By H. v. PECHMANN and L. FROBENIUS (*Ber.*, **27**, 672—673).—The sodium salt of paranitrodiazobenzene, $NO_2\cdot C_6H_4\cdot NNa\cdot NO$, recently described by Schraube and Schmidt (this vol., i, 237), has been prepared independently by the authors; its constitution is shown by the production of a highly unstable crystalline compound with aniline, which is being further investigated. With methylic iodide, paranitrophenylnitrosamine, $NO_2\cdot C_6H_4\cdot NMe\cdot NO$, is formed. *Silver paranitrodiazobenzene*, $NO_2\cdot C_6H_4\cdot N:NOAg$, is obtained

from the sodium salt by the action of silver nitrate, and on treatment with methylic iodide yields *paranitrodiazobenzene methyl ether*, $NO_2 \cdot C_6H_4N \colon NOMe$, which crystallises in almost colourless needles, and melts at 83°. On boiling with dilute acids, nitrogen is evolved, and paranitrophenol is formed. By the action of aniline in alcoholic solution, paranitrodiazoamidobenzene, $NO_2 \cdot C_6H_4 \cdot N \colon N \cdot NHPh$, is obtained, whilst, on treatment with phenol paranitrobenzeneazophenol, $NO_2 \cdot C_6H_4 \cdot N \colon N \cdot C_6H_4 \cdot OH$, is formed the *acetyl-derivative* of which crystallises in flesh-coloured needles, and melts at 146°.   J. B. T.

Aromatic Bisdiazo Compounds. By H. V. PECHMANN and L. FROBENIUS (*Ber.*, **27**, 703—706; compare *Ber.*, **27**, 651, preceding abstracts) —Nitrosoacetanilide, or nitrosobenzanilide, reacts with aniline in the presence of free alkali to form *bisdiazobenzeneanilide* (benzenediazoanilinediazobenzene), $NPh(N \colon NPh)_2$. The same compound may be obtained by treating aniline dissolved in methylic alcohol with a solution of diazobenzene chloride in the same solvent in the presence of sodium methoxide, at a low temperature. It forms yellow, lustrous plates, and is sparingly soluble in ether and alcohol, readily in benzene and chloroform. When heated to 80—81°, it explodes with a loud report, and also explodes when struck. Its constitution is shown by the fact that, when boiled with a mineral acid, it decomposes quantitatively, according to the equation $NPh(N \colon NPh)_2 + 2H_2O = 2PhOH + 2N_2 + NH_2Ph$. The compound can be preserved without alteration.

Bisparadiazotolueneparatoluidide, $C_7H_7 \cdot N(N \colon N \cdot C_7H_7)_2$, may be obtained from nitrosoacetotoluidide or nitrosobenzotoluidide; by the direct action of diazoparatoluene chloride on paradiazoamidotoluene in alcoholic solution; or by the action of diazotoluene chloride on toluidine. It forms sulphur yellow needles, and is sparingly soluble in ether, readily in benzene and chloroform. It explodes when vigorously struck, or when heated, but less violently than the aniline compound. It may be heated in a melting point tube to 88°, and then detonates gently. It is decomposed by acids in a similar manner to the aniline compound.   A. H.

Benzenediazoic Acid from Nitryl Chloride and Aniline. By E. BAMBERGER (*Ber.*, **27**, 668—671).—Having obtained benzenediazoic acid from nitric anhydride and aniline (this vol., i, 239), the author has attempted to prepare it from nitryl chloride and aniline, the results confirm the doubts as to the existence of nitryl chloride expressed by others; in any case it is not obtained pure by any of the methods described below. Benzenediazoic acid is not formed by the action of nitric oxide, nitrous anhydride, nitric acid, or nitrosyl chloride on aniline. "Nitryl chloride," prepared by Williamson's method from chlorosulphuric acid and potassium nitrate, was obtained as a colourless gas, and was allowed to act on aniline in ethereal solution at low temperatures, the yield of benzenediazoic acid was 0·3 gram from 41 grams of aniline; the following substances were also formed: diazoamidobenzene, orthonitraniline, azobenzene, and probably paranitraniline, and diazobenzene salts. The "nitrylic

chloride" formed by Exner's method from silver nitrate and phos-
phorus oxychloride is a reddish-brown gas; with aniline (50 grams)
it yields benzenediazoic acid (0·05 gram), diazoamidobenzene, and
possibly traces of orthonitraniline and paranitraniline.   Hasenbach's
" nitrylic chloride" from nitrogen peroxide and chlorine appears to
consist chiefly of nitrosyl chloride, as, on treatment with aniline, it
yields diazoamidobenzene, aniline nitrate and hydrochloride, azo-
benzene, diazobenzene nitrate and hydrochloride, and possibly ortho-
nitraniline. Benzenediazoic acid could not be detected with certainty.
Aniline hydrochloride, diazobenzene chloride, and diazoamidobenzene
are the sole products formed by the action of nitrosyl chloride on
aniline. Nitric peroxide or nitric acid (b. p. 86°) and aniline yield
aniline nitrate, diazobenzene nitrate, diazoamidobenzene, and in small
quantity ortho- and para-nitraniline.   With nitrous anhydride, the
products were the same, with the exception of ortho- and para-
nitraniline. Nitric acid and nitrous anhydride both appear to yield
traces of benzenediazoic acid.   J. B. T.

Tertiary and Quaternary Aromatic Hydrazines. By C. D.
HARRIES (*Ber.*, **27**, 696—702).—Tertiary hydrazines can be prepared
from the formyl-derivatives of the secondary hydrazines, but not
from the acetyl-derivatives, because the acetyl-group cannot be
removed without the decomposition of the molecule.

Phenylmethylformylhydrazine, $NMe·Ph·NH·CHO$, forms a white
crystalline mass melting at 50—51°.   It has a not unpleasant smell,
boils at 183—185° under a pressure of 11 mm., and is soluble in
alcohol, but scarcely in water.

Phenyldimethylformylhydrazine, obtained by the action of methylic
iodide on the sodium compound of this formyl-derivative, is a colour-
less liquid ; it boils at 147—148° (7 mm.), and is very sparingly soluble
in dilute acids.

Phenyldimethylhydrazine, $NMePh·NHMe$, is a bright green, highly-
refractive liquid, which boils at 93—94° (7 mm.).   It reduces silver
nitrate solution in the cold, but scarcely acts on Fehling's solution
even on boiling.   It is very soluble in all solvents except water, and
gives a rose-red coloration with bleaching powder solution.   The
hydrobromide and *hydriodide* crystallise well, whilst the *hydrochloride*
and *sulphate* are very soluble.   The *ferrocyanide* crystallises in rhombic
tablets, and is employed in the purification of the base.

Phenyldimethylnitrosohydrazine, obtained by the action of sodium
nitrate on a solution of the base in hydrochloric acid, is a dark red,
thick oil, which gives Liebermann's reaction ; it decomposes when dis-
tilled in a vacuum, the base being largely regenerated.   The nitroso-
compound is scarcely attacked by continued boiling with aqueous soda,
and does not undergo intramolecular change when treated with alco-
holic hydrochloric acid.   On reduction, it yields methylaniline and
methylhydrazine.

Phenyldimethylbenzoylhydrazine crystallises from alcohol in large,
feathery plates melting at 103—104°.

Phenyltrimethylhydrazine, $NMePh·NMe_2$, is obtained by the action
of methylic iodide on phenyldimethylhydrazine.   It forms a colour-

less oil, which boils at 93—94° (8 mm.), and has a characteristic odour of cedar wood. It gives no coloration with bleaching powder, does not reduce Fehling's solution at all on boiling, but reduces silver solution in the cold. The base easily decomposes with formation of dimethylaniline, and probably dimethylamine. The only salt which has been obtained in the solid state is the *ferrocyanide*.

Phenyldimethylmethylazonium iodide, $NMe_2PhI \cdot NHMe$, is readily soluble in water, and forms thin plates melting at 145°, after becoming brown at 80°.

Phenylmethylethylformylhydrazine boils at 169° (12 mm.), and is a colourless oil. *Phenylmethylethylhydrazine* boils at 101—102° (9 mm.). The *hydrobromide* forms large, blunted prisms. The *nitrosocompound* is a thick, dark red oil, which on reduction yields methylhydrazine and ethylhydrazine. A. H.

Acid Imides and Hydrazine Hydrate. By R. v. ROTHENBURG (*Ber.*, **27**, 691—692).—*Amidophthalimide*, $CO {<}{C_6H_4 \atop O}{-}{>} C\!:\!N \cdot NH_2$, is prepared by heating phthalimide with hydrazine hydrate or acetate in alcoholic solution; it is a colourless, sparingly soluble powder, melting at 250—251°.

Benzalamidophthalimide, $CO {<}{C_6H_4 \atop O}{-}{>} C\!:\!N \cdot N\!:\!CHPh$, is formed by the action of benzaldehyde on the preceding compound in aqueous solution at the ordinary temperature; it is almost completely insoluble, remains unchanged at 250°, and is resolved into its constituents on treatment with acids or alkalis.

Isopropyleneamidophthalimide, $CO {<}{C_6H_4 \atop O}{-}{>} C\!:\!N \cdot N\!:\!CMe_2$, is obtained by heating amidophthalimide with acetone; it melts at 260°, and is sparingly soluble. Hydrazine derivatives of succinimide could not be prepared; this, in the author's opinion, points to the formula, $CO {<}{C_6H_4 \atop O}{-}{>} C\!:\!NH$ for phthalimide, whilst succinimide is probably symmetrical. J. B. T.

Oxindophenolic Colouring Matters from Gallanilide and Galloparatoluidide. By P. CAZENEUVE (*Bull. Soc. Chim.*, [3], **11**, 85—87).—The colouring matters from gallanilide have been already described (Abstr., 1893, i, 510). Those from its homologue are exactly analogous, and in physical respects almost identical.
Jn. W.

Diacid Anilides. By G. TASSINARI (*Gazzetta*, **24**, i, 61—62).— The author was endeavouring to prepare diacid anilides when he was anticipated by Kay (this vol., i, 76), whose results he confirms.

On heating a mixture of formanilide, acetic anhydride, and sodium acetate, a crystalline product is ultimately obtained, which could not be freed from acetanilide; for this reason, possibly, the analytical results do not agree with those of formacetanilide.

Diacetanilide may be prepared by treating acetanilide with acetic anhydride; it is instantly decomposed by aqueous ammonia, giving

acetanilide and ammonium acetate, whilst on treatment with ammonia dissolved in anhydrous ether, it yields acetamide and acetanilide. It is also conveniently prepared by the action of acetic chloride on sodioacetanilide, using benzene as a diluent; when heated at 40° with decinormal soda solution, one acetyl group is removed quantitatively.

Parabromodiacetanilide forms small crystals melting at 69—70°; it behaves similarly to diacetanilide with decinormal soda, and with aqueous and dry ammonia.   W. J. P.

The Formoïns. By W. ABENIUS (*Ber.*, **27**, 706—719).—Benzoyl-formoin, when treated in alcoholic solution with hydroxylamine hydrochloride, yields, in addition to other products, a substance of the formula $C_{18}H_{16}O_4$ (Abstr., 1892, 69). This compound is *β-ethyl-benzoylformoïn*, OH·CPh:C(OEt)·CO·COPh, and is quantitatively formed by the action of hydrogen chloride on an alcoholic solution of benzoylformoïn; with alkalis it gives yellow salts, which are soluble in dilute, but not readily in concentrated, aqueous alkalis. Nitric acid converts it into diphenyltetraketone. When it is boiled with acetic anhydride, *acetyl-β-ethylbenzoylformoïn*,

OAc·CPh:C(OEt)·CO·COPh,

is formed; this crystallises from alcohol in groups of short, colour-less prisms melting at 121—122°, and is readily hydrolysed by aqueous potash or by the addition of strong hydrochloric acid to its alcoholic solution, the β-ethyl compound being quantitatively re-generated. *Benzoyl-β-ethylbenzoylformoïn*,

COPh·O·CPh:C(OEt)·CO·COPh,
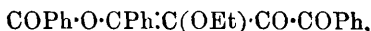
separates from alcohol in aggregates of small, white crystals melting at 147°, and is very readily hydrolysed. The *paratoluyl-derivative*, $C_7H_7·COO·CPh:C(OEt)·CO·COPh$, forms long, colourless crystals, which dissolve readily in alcohol, benzene, and ether, and melt at 125—126°. On hydrolysis, it is quantitatively converted into ethyl-benzoylformoïn. The *cuminoyl-derivative*,

$C_9H_{11}·COO·CPh:C(OEt)·CO·COPh$,
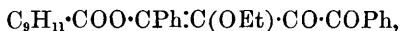
forms short prisms melting at 108—109°; it is only slightly solu-ble in cold alcohol. On hydrolysis, it is, like the other derivatives, quantitatively converted into ethylbenzoylformoïn.

The fact that all these acid derivatives of β-ethylbenzoyl-formoïn are converted by hydrolysis into ethylbenzoylformoïn seems to show that they are derived from the dihydroxyl form of benzoylformoïn, OH·CPh:C(OH)·CO·COPh, and not from the alco-holic form, COPh·CH(OH)·CO·COPh. This view is confirmed by the reactions of the other derivatives containing two acid or alkyl groups, and by the fact that ethylbenzoylformoïn itself combines with phenylcarbimide to form a crystalline *additive product*,

NHPh·COO·CPh:C(OEt)·CO·COPh,
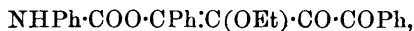
which forms nacreous plates melting at 159—160°.

β-Methylbenzoylformoïn, OH·CPh:C(OMe)·CO·COPh, is prepared in

a similar manner to the ethyl derivative, and is readily soluble in alcohol, ether, &c. It resembles the ethyl compound in its reactions. The *acetyl-derivative*, OAc·CPh:C(OMe)·CO·COPh, crystallises in short, lustrous, colourless prisms melting at 95°. The *cuminoyl-derivative*, C_9H_{11}·COO·CPh:C(OMe)·CO·COPh, forms spherical aggregates of short prisms, and melts at 112°.

β-Amylbenzoylformoïn is prepared in a similar manner, and is readily soluble in alcohol. *β-Benzylbenzoylformoïn* crystallises from alcohol in yellow needles melting at 182—183°. *β-Ethylparatoluylformoïn*, C_7H_7·C(OH):C(OEt)·CO·COPh, is formed when an alcoholic solution of paratoluylformoïn is saturated with hydrogen chloride; it crystallises from light petroleum in thin plates melting at 140—146°. The *benzoyl derivative*, C_7H_7·C(O·COPh):C(OEt)·CO·COPh, is amorphous, and, on hydrolysis, yields benzoic acid and β-ethylparatoluylformoïn.

αβ-Diethylbenzoylformoïn, OEt·CPh:C(OEt)·CO·COPh, is prepared by boiling an alcoholic solution of β-ethylbenzoylformoïn with sodium ethoxide and ethylic iodide. It separates from hot alcohol in lustrous crystals melting at 83—84°. It is perfectly neutral to dilute alkalis and acids, and is converted by nitric acid into a resin.

α-Ethylbenzoylformoïn, OEt·CPh:C(OH)·CO·COPh, is formed by the action of concentrated sulphuric acid on the foregoing compound; it crystallises from alcohol in short, yellow, monosymmetric prisms melting at 137—138°, is readily soluble in dilute alkalis, and is converted by nitric acid into a resinous mass. When its solution in alcohol is saturated with hydrogen chloride, it is reconverted into diethylbenzoylformoïn. The *acetyl derivative*,

$$\text{OEt·CPh:C(OAc)·CO·COPh,}$$

is formed by the action of acetic anhydride on the α-ethyl compound, together with another substance which has not been further examined. It crystallises from alcohol in colourless prisms melting at 114—115°.

α-Methyl-β-ethylbenzoylformoïn, OMe·CPh:C(OEt)·CO·COPh, is prepared by boiling β-ethylbenzoylformoïn in alcoholic solution with sodium methoxide and methylic iodide; it separates from alcohol in small, crystalline groups, and melts at 105°. It is converted by concentrated sulphuric acid into *α-methylbenzoylformoïn*, which has not yet been further examined.

Diacetylbenzoylformoïn, OAc·CPh:C(OAc)·CO·COPh, is obtained by boiling benzoylformoïn with acetic anhydride; it crystallises from alcohol in rosettes of small plates melting at 158°, and is readily converted by hydrolysis into acetic acid and benzoylformoïn.

A substance isomeric with this diacetyl-derivative seems to be formed at the same time; it melts at 124—125°, but was obtained in such small quantity that it could not be examined.

The *bromo-derivative*, OEt·CPhBr·CO·CO·COPh, is formed by treating with bromine diethyl- or α-ethyl-benzoylformoïn suspended in water. A red oil is formed, which is probably an additive product containing 2 atoms of bromine, but this soon solidifies, the same compound being finally formed in both cases. It crystallises from a mixture of benzene and light petroleum in light yellow,

lustrous tablets or prisms melting at 101—102°.   It is not soluble in alkalis, but is decomposed if boiled with them.   It seems probable that an additive compound is first formed, and that then the elements of ethylic bromide or hydrogen bromide are eliminated, the final product being the same in both cases.

Notwithstanding these reactions, which point to the dihydroxyl formula for benzoylformoïn, its formation from phenylglyoxal, $COPh \cdot CHO$, by condensation in the presence of alcoholic potassium cyanide, and the production of tetraketone derivatives from it by oxidation, seem to indicate that the free compound only contains one hydroxyl group, the dihydroxyl formula being that of a tautomeric form.   A. H.

Aromatic Tetraketones.   By H. G. Söderbaum (*Ber.*, **27**, 658—663; compare Abstr., 1893, i, 169).—1 : 2 : 4-*Xyloylformoxime*,

$$C_6H_3Me_2 \cdot CO \cdot CH\text{:}NOH \; [= 1 : 2 : 4],$$

is obtained by mixing 1 : 2 : 4-xylyl methyl ketone, sodium, amylic nitrite, and alcohol, and, after the action has taken place, dissolving the sodium salt thus formed in ice cold water, and precipitating with acetic acid; it crystallises in short prisms or thick plates, and melts at 121°.   The *acetyl compound*, $C_6H_3Me_2 \cdot CO \cdot CH(OH) \cdot NAc \cdot OH$, is obtained by treating it with acetic chloride, and, after drying on a porous plate the hydrochloride thus formed, decomposing it with ice cold water.   It crystallises in long, white needles, and melts at 130—131°.

1 : 2 : 4-*Xyloylformoïn*, $C_6H_3Me_2 \cdot CO \cdot CH(OH) \cdot CO \cdot CO \cdot C_6H_3Me_2$, is obtained by treating the above acetyl compound, dissolved in alcohol, with potassium cyanide.   It is a crystalline, sulphur-yellow substance, sinters at 138°, and melts at 146°.   It cannot be recrystallised without decomposition, and, when dissolved in benzene, decomposes into two acid compounds melting at 92° and 163—164°, which are probably orthoxylylglyoxylic acid and metaparadimethylbenzoic acid respectively.

1 : 2 : 4-*Dixylyltetraketone monhydrate*,

$$C_6H_3Me_2 \cdot CO \cdot C(OH)_2 \cdot CO \cdot CO \cdot C_6H_3Me_2,$$
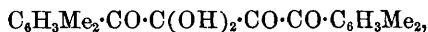
is obtained by treating the above formoïn with nitric acid.   It crystallises in short, yellow prisms, sinters at 103°, melts at 108° with decomposition, and gradually decomposes when allowed to remain in a dessicator.

1 : 4 : 2-*Xyloylformoxime*, $[Me_2 : (CO \cdot CH\text{:}NOH) = 1 : 4 : 2]$, obtained, together with isoxylylic acid, in the same way as the 1 : 2 : 4-compound, crystallises in beautiful, pale yellow needles, and melts at 63°·   The *acetyl-compound* crystallises in hard, white nodules, melts at 135—136°, and, when dissolved in alcohol, gives an intense red coloration with ferric chloride.

1 : 4 : 2-*Xyloylformoïn* crystallises in microscopic prisms, sinters at 160°, melts at 164—168°, and decomposes, when allowed to remain in contact with its solvents, yielding a compound which melts at 125—130°, probably isoxylylic acid.

1 : 4 : 2-*Dixylyltetraketone monhydrate* crystallises in beautiful, bright

yellow prisms, reddens at 100°, softens at 105°, and melts at 109—110° with decomposition.

The dixylyltetraketones of the ortho- and para-series, like the corresponding phenyl, tolyl, and bromophenyl compounds, yield monhydrates, whereas dimetaxylyltetraketone exists either in the unhydrated form or yields a dihydrate.　　　　　　　　E. C. R.

Isomerism of Nitrobenzoic acids. By O. DE CONINCK (*Compt. rend.*, **118**, 471—473).—The nitrobenzoic acids, like the amidobenzoic acids, can be groups in pairs according to their solubilities in different solvents. In water and dilute alcohol, the ortho- and meta-acids are easily soluble; the para-acid is only slightly soluble. In ether, the order is the same, but in all three cases the numerical values are much higher. With chloroform and benzene, the para-derivative is very slightly soluble, the meta-derivative is easily soluble, whilst the ortho-derivative shows intermediate solubility. In carbon bisulphide and light petroleum, the meta-acid is the most soluble, whilst the ortho- and para-acids are much less soluble.
　　　　　　　　　　　　　　　　　　　　　　　　C. H. B.

Guaiacolglycollic acid. By A. CUTOLO (*Gazzetta*, **24**, i, 63—64). —*Guaiacolglycollic acid*, $OMe \cdot C_6H_4 \cdot O \cdot CH_2 \cdot COOH$, is prepared by heating guaiacol with monochloracetic acid on the water bath, and subsequently adding soda and acidifying. It forms beautiful, white needles melting at 120°, and is soluble in alcohol and in water. The *barium* salt crystallises in small, prismatic needles containing $3H_2O$, and is very soluble in water. The *silver* salt is obtained in beautiful needles, which become red on exposure to light.　　　　　W. J. P.

Synthesis of the Cresolcoumarins. By A. CURATOLO and G. PERSIO (*Gazzetta*, **24**, i, 45—48).—On heating the sodium cresolglycollates with salicylaldehyde and acetic anhydride, for six hours at 150—160°, condensation occurs, and the corresponding cresolcoumarins are formed. The product is extracted with boiling water and sodium carbonate solution, and the residue purified by dissolving in potash, and precipitating with hydrochloric acid.

Orthocresolcoumarin, $C_6H_4 < ^{O-CO}_{CH:C \cdot C_6H_4Me}$, which crystallises in lustrous, micaceous scales melting at 100—101°, is very soluble in alcohol or ether.

Meta- and *para-cresolcoumarin* resemble the ortho-isomeride in appearance and behaviour towards solvents; they melt at 106—107° and 113—114° respectively. All three isomerides yield coumaric acid on prolonged boiling with 50 per cent. potash.　　　　　　W. J. P.

Action of Bleaching Powder and Hypochlorous acid on Quinones.—By T. ZINCKE and W. SCHMIDT (*Ber.*, **27**, 733—744; compare Abstr., 1892, 1229—1232).—The *lactone* of *α-dichloro-β-hydroxyorthohydrocinnamocarboxylic acid*,

$$COOH \cdot CCl_2 \cdot CH <^{O-}_{C_6H_4} > CO,$$
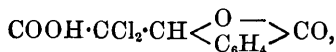
is obtained by the action of bleaching powder solution on monochloro-β-naphthaquinone. It crystallises in small, fine, prismatic needles melting at 157°, is insoluble in light petroleum, and crystallises from hot water in tablets containing $1H_2O$. The *sodium salt*, $C_{10}H_5Cl_2O_4Na$, forms crystalline granules. The *methylic salt* separates from a mixture of ether and light petroleum in large, colourless crystals, melting at 77°. The lactone, by reduction, is converted into ortho-hydrocinnamocarboxylic acid. The *lactone* of *α-chlorobromo-β-hydro-oxyorthohydrocinnamocarboxylic acid*, $COOH \cdot CClBr \cdot CH{<}^{O---}_{C_6H_4}{>}CO$, is prepared like the dichloro-compound by the action of bleaching powder on monobromo-β-naphthaquinone; it forms colourless, prismatic needles, melts at 175°, and is less soluble than the dichloro-compound.

The dichloro-lactone is accompanied by a monochlorophthalic acid melting at 158°, the constitution of which has not yet been ascertained.

The two lactones just described are converted by the action of aqueous soda or baryta into the *lactone* of *α-keto-β-hydroxyortho-hydrocinnamocarboxylic acid*, $COOH \cdot CO \cdot CH{<}^{O---}_{C_6H_4}{>}CO$; this crystallises in fascicular groups of fine needles and melts and decomposes at 246°. It is sparingly soluble in benzene, but readily in alcohol or hot water, and dissolves in alkalis with formation of the salts of the bibasic acid. The *barium salt*, ${}^{C_6H_4-----COO}_{CH(OH) \cdot CO \cdot COO}{>}Ba + H_2O$, is a yellow crystalline precipitate, which yields the lactone when decomposed by acids. The *oxime*, $C_{10}H_6(N \cdot OH)O_4$, forms small, colourless prisms, melting at 167—168°.

When the above lactone is dissolved in sodium carbonate and treated with sodium hypochlorite, it is converted into the *lactone* of *ortho-hydroxyhomophthalic acid*, $COOH \cdot CH{<}^{O---}_{C_6H_4}{>}CO$; the latter may also be obtained in a similar manner from isocoumarincarboxylic acid. It crystallises in silky plates, is readily soluble in water and alcohol, and melts at 151—152°. The *methylic salt* forms rosettes of broad needles, melting at 54—55°. On reduction, the lactonic acid is converted into homophthalic acid.

Dichloro-β-naphthaquinone is converted by bleaching powder into dichloroketohydroxyhydrindenecarboxylic acid, dichlorodiketohydrindene and trichloracetophenonecarboxylic acid, very little of the first named product being formed if excess of bleaching powder be employed.

The formulæ given above are the most probable, but they have not been proved with certainty. The action of bleaching powder on the chloro- and bromo-derivatives of β-naphthaquinone resembles that of the same reagent on nitronaphthaquinone and differs entirely from its action on β-naphthaquinone itself.   A. H.

Derivatives of Benzenesulphonamide and Hydrazine. By O. HINSBERG (*Ber.*, **27**, 598—602).—When benzenesulphonamide is suspended in water, and treated with sodium nitrite and excess of

sulphuric acid, part is converted into dibenzenesulphonehydroxyl-amine, $(C_6H_5 \cdot SO_2)_2NOH$; (König's dibenzsulphydroxamic acid), and part into benzenesulphonic acid, whilst some remains unchanged. If benzenesulphonamide is dissolved in the equivalent amount of aqueous soda, excess of sodium carbonate first added, and then, to the cooled solution, a hydrochloric acid solution of diazobenzene chloride, *benzenesulphonediazobenzeneamide*, $C_6H_5 \cdot SO_2 \cdot NH \cdot N_2Ph$, separates in yellow needles; it melts and decomposes at 102°. It is decomposed when warmed with dilute acids or alkalis, the products including benzenesulphonamide, phenol, and nitrogen ; it also yields a bromine additive compound.

Benzenesulphonehydrazine cannot be obtained by reducing ben-zenesulphonenitramide, $C_6H_5 \cdot SO_2 \cdot NH \cdot NO_2$, by any of the usual methods ; these yield the sulphonamide instead. Its *benzal derivative*, $C_6H_5 \cdot SO_2 \cdot NH \cdot N \colon CHPh$, can, however, be obtained in small quantity by mixing the potassium salt of benzenesulphonenitramide with an equal weight of zinc dust, suspending the mixture in water, and, after the lapse of half an hour, adding gradually about half the weight of acetic acid to the cooled solution, filtering, acidifying with hydrochloric acid, filtering again after a time, and finally shaking with benzaldehyde. This derivative forms a yellow crystalline pre-cipitate, and melts at 110°; it was not found possible to isolate the hydrazine from it, as acids decompose it with liberation of benzalde-hyde and phenyl mercaptan ; the other products formed, besides the hydrazine, are the sulphonamide, sulphinic acid, and sulphonehydr-oxylamine. *Dibenzenesulphonehydrazine*, $(C_6H_5 \cdot SO_2)_2N \cdot NH_2$, may be obtained by dissolving hydrazine sulphate in a little water, cooling the solution and then adding excess of potash and benzenesulphochloride ; it forms white needles, and melts with decomposition at 245°. It yields a potassium salt which is only sparingly soluble in aqueous potash, and which decomposes when heated into nitrogen and benzenesulphonic acid.   C. F. B.

Action of Benzenesulphonic acid on Potassium Iodide. New Class of Organic Periodides. By J. H. KASTLE and H. H. HILL (*Amer. Chem. J.*, 16, 116—122).

—While studying the action of benzenesulphonic acid on potassium iodide, these sub-stances were heated together in molecular proportion for some time in aqueous solution. The solution became deep red-brown, and after two months was found to contain a large quantity of opaque-green crystals of metallic lustre. These crystals dissolved readily in water, and, on boiling the solution, it was decolorised, large quantities of iodine being evolved. Analysis led to the probable formula $(C_6H_5 \cdot SO_3K)_5, KI, I_5$. This substance is best produced by mixing a strong aqueous solution of potassium benzenesulphonate with the required quantity of iodine dissolved in the smallest possible quantity of potassium iodide solution. *Potassium benzenesulphonate periodide* $(C_6H_5 \cdot SO_3K)_5, KI, I_5$, crystallises in opaque, thin, much elongated, rectangular prisms, of a brilliant, greenish-bronze lustre. They rapidly lose iodine, and their surfaces become dulled. Five-sixths of the iodine appears to be very loosely held. *Sodium benzene-*

sulphonate periodide, $(C_6H_5 \cdot SO_3Na)_5NaI,I_4$, obtained in like manner, closely resembles the potassium salt in appearance and behaviour. The iodine is present, however, in smaller proportion, four-fifths being present in a loosely combined state. A similar *barium salt*, $[(C_6H_5 \cdot SO_3)_2Ba]_5,BaI_2,I_{10}$, forms fine needles of greenish-bronze lustre.   L. T. T.

Thiosulphonic acids and Sulphinic acids. By H. LIMPRICHT (*Annalen*, **278**, 239—260).—*Metanitrobenzenethiosulphonic acid*, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot SH$, is formed as barium salt when barium hydroxide, suspended in water, is thoroughly saturated with hydrogen sulphide, and finely-pulverised nitrobenzenesulphonic chloride added. The solution is evaporated, and the residue treated with 95 per cent. alcohol, the precipitated barium chloride being filtered off, and the filtrate evaporated. The residue is dissolved in water, and the solution, on remaining over concentrated sulphuric acid, yields crystals of the impure barium salt. A solution of the latter is treated (warmed ?) with dilute sulphuric acid, the precipitate of barium sulphate and sulphur filtered off, and the filtrate containing nitrobenzenesulphinic acid treated with dilute ammonium sulphide, whereby ammonium nitrobenzenethiosulphonate is formed, from which the pure barium salt is readily obtained; it crystallises with $2\frac{1}{2}H_2O$. The free acid forms white plates, and melts at 164°.

The preparation of metanitrobenzenesulphinic acid, $NO_2 \cdot C_6H_4 \cdot SO_2H$, is best carried out as already described (Abstr., 1892, 475; 1893, i, 168); a small quantity of metamidobenzenesulphonic acid is simultaneously formed. The pure nitro-acid melts at 98°, and gives a deep-blue coloration with sulphuric acid on addition of a drop of phenol. The *potassium* salt is anhydrous, the *sodium* salt crystallises with $2H_2O$, the *barium* salt with 4 and with $1H_2O$, and the silver salt is so sparingly soluble in water that it is available for the purification and detection of the acid. The *sulphobromide* melts at 68°, and the *anilide* at 122°. When the *sodium* salt is heated with alcohol and ethylic bromide in a sealed tube at 130°, the *compound* $NO_2 \cdot C_6H_4 \cdot SO_2Et$ is formed; it melts at 100°. With ethylenic bromide under like circumstances, a compound is obtained melting at 226°; it is probably the disulphone, $C_2H_4(SO_2 \cdot C_6H_4 \cdot NO_2)_2$ (Otto, *Ber.*, **13**, 1275). Nitrobenzenesulphinic acid does not react with phosphoric chloride as stated by Otto (*Annalen*, **141**, 374), but under these circumstances nitrophenylic bisulphoxide (see below) is formed. The *hydrazine*, $NO_2 \cdot C_6H_4 \cdot SO_2H,N_2H_3Ph$, melts at 131°.

Phenylnitrobenzenesulphazide, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot N_2H_2Ph$, is obtained by mixing phenylhydrazine and nitrobenzenesulphonic chloride in alcoholic solution; it forms bright yellow needles, melts at 154°, and decomposes into nitrogen, benzene, and nitrobenzenesulphinic acid when warmed with alkalis.

Metamidobenzenethiosulphonic acid, $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot SH$, is obtained by dropping nitrobenzenesulphonic chloride into a concentrated aqueous solution of ammonium hydrosulphide; it crystallises in white prisms, and melts at 167°. When warmed with acids, ferric chloride, or potassium iodide, half the sulphur is precipitated, in the latter

case with the liberation of iodine; the sulphur thus obtained being insoluble in carbon bisulphide. The alkali salts of the acid just described are very soluble in water and alcohol. When a solution of the sodium salt is reduced by sodium amalgam, metamidobenzene-sulphinic acid, $NH_2 \cdot C_6H_4 \cdot SO_2H$, is formed; at 210° it carbonises without melting. The alkali salts are so soluble in water and alcohol that they cannot be obtained in crystals.

Nitrophenylic bisulphoxide, $S_2O_2(C_6H_4 \cdot NO_2)_2$, is formed, together with nitrobenzenesulphonic acid, by warming nitrobenzenesulphinic acid with acids; it crystallises in yellowish needles, and melts at 123°. If the bisulphoxide is boiled with alkalis, a salt of nitro-benzenesulphinic acid separates, together with a resinous substance, from which *nitrophenylic bisulphide*, $(NO_2 \cdot C_6H_4)_2S_2$, may be extracted by boiling alcohol; this forms yellow crystals, melts at 82°, and gives a red coloration with concentrated sulphuric acid and an indigo-blue coloration with anhydrosulphuric acid.

Amidophenylic bisulphide is prepared by reducing the nitro-compound with ammonium sulphide; its salts do not crystallise well. Amidophenylic bisulphoxide, $S_2O_2(C_6H_4 \cdot NH_2)_2$, is obtained, together with amidobenzenesulphonic acid, by warming amidobenzenesulphinic acid with acids; it was not obtained in the pure state.

In preparing metanitrophenyltolylsulphone, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot C_6H_4Me$ (compare Otto, *Ber.*, 11, 2066), by heating together metanitrobenzene-sulphonic chloride, aluminium chloride, and carbon bisulphide, it was noticed that the yield was extremely small, nitrophenylic bisulphoxide and other compounds being produced. The sulphoxide is undoubtedly a secondary product formed by the action of acids on nitrobenzene-sulphinic acid, and, in proof that the latter is the first product, it is shown to be produced when nitrobenzenesulphonic chloride, alu-minium chloride, and carbon bisulphide are heated together in a reflux apparatus for 24 hours; a compound of nitrobenzenesulphinic acid with aluminium chloride was isolated, for which the formula $(NO_2 \cdot C_6H_4 \cdot SO_2)_3Al_2Cl_2$ is given. The conditions for the preparation of metanitrophenyltolylsulphone, as above, have not been ascertained; the compound melts at 93°, and yields *nitrophenylsulphonebenzoic acid*, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot C_6H_4 \cdot COOH$, when oxidised with chromic acid; this acid melts at 269°, and its *barium* salt crystallises with $2H_2O$.

A. R. L.

Oxidation of Reduced Indoles. By M. KANN and J. TAFEL (*Ber.*, **27**, 826—827).—Dihydro-2'-methylindole and dihydro-3'-methylindole are converted, to the extent of about 50 per cent., into 2'-methylindole and 3'-methylindole (skatole) respectively by distilla-tion with silver sulphate (1 mol. : 2 mol. indole). The oxidation cannot be accomplished by the action of mercuric acetate.

J. B. T.

Two Stereoisomeric Hydrazones of Benzoïn. By A. SMITH and J. H. RANSOM (*Amer. Chem. J.*, **16**, 108—117).—By acting on an alcoholic solution of benzoïn with phenylhydrazine (1 mol.) Pickel obtained (Abstr., 1886, 545) benzoïn monophenylhydrazone, $C_{20}H_{18}N_2O$,

melting at 155°. The authors find, however, that if the alcoholic mixture is heated on the water bath for three to four hours, and then allowed to cool, a new isomeric *β-hydrazone*, melting at 106°, is mixed with the other product. The two substances may be separated from one another by dissolving them in boiling light petroleum, the β-compound separating out first on cooling. The best mode of preparing the two isomerides is, however, to dissolve 20 grams of benzoïn and 10 grams of phenylhydrazine in 200 c.c. of 95 per cent. alcohol, warm the solution for three or four hours on the water bath, and then set it aside for 12 hours. A large crop of crystals of the β-hydrazone will then be formed, and, if the liquid is filtered off and well shaken for a few minutes, it deposits the α-form entirely free from admixture with the β-form. If benzoïn and phenylhydrazine, in molecular proportion, are cautiously heated together without any solvent, a thick oil is produced, consisting almost wholly of the β-form.

Both forms crystallise in small, white needles, which do not change colour on exposure to air or sunlight, the α-form yielding thick, the β-form thin, monoclinic prisms. Both are soluble in warm, light petroleum, more so in warm alcohol, and very soluble in benzene. Both dissolve readily in warm acetic acid, but the β-form is only recoverable therefrom as an oil. Even prolonged heating with alcohol converts the β-compound into this oil. The β-compound is much more soluble in all these solvents than the α-form. Both are insoluble in alkalis and dilute mineral acids; strong sulphuric acid dissolves both with a deep red coloration, which turns green on the addition of a crystal of potassium dichromate; both are converted into tarry products by strong hydrochloric or nitric acids, or by acetic chloride; both reduce Fehling's solution when warmed with it. When pure, the α-hydrazone melts at 106°, the β- at 158—159°. Determinations of the molecular weight by Raoult's method showed that each has a simple molecule. Benzaldehyde yields the same compound, $C_{47}H_{36}N_4$. with each; it crystallises in small, white plates and melts at 215—216°, but has not been further investigated. Phenylhydrazine in acetic acid solution yields with each the same benziledi-phenylhydrazone melting at 225°. The β-hydrazone is converted into the α-form by boiling it for some time in alcoholic solution with phenylhydrazine (2 mols.). L. T. T.

Condensation of Phthalides with Phenol. By G. ERRERA and G. GASPARINI (*Gazzetta*, **24**, i, 70—81).—*Imidophenolphthalein*, $CO < {}^{C_6H_4}_{NH-} > C(C_6H_4 \cdot OH)_2$, is formed on heating a mixture of phthalimide, phenol, and stannic chloride at 115—120° for five hours; it is ultimately obtained in hard, colourless, lustrous, acicular crystals containing 1 mol. of benzene of crystallisation, which is lost on exposure to the air. It melts at 2?2°, undergoing slight decomposition, and does not combine with hydroxylamine; the latter fact is in favour of Bernthsen and Friedländer's view, that free phenolphthaleïn has a quinonoïd structure, whilst its metallic derivatives are salts of a true carboxylic acid. Imidophenolphthaleïn is insoluble in benzene or dilute mineral acids, but readily soluble in alkalis, alkali carbonates,

alcohol, or acetic acid. It does not yield Burkhardt's diimidophenolphthaleïn (Abstr., 1878, 836) when heated with aqueous ammonia in a sealed tube at 160—170°; this is perhaps accounted for by the fact that the authors were unable to prepare Burkhardt's diimidophenolphthaleïn.

Diacetylimidophenolphthaleïn, $CO<^{C_6H_4}_{NH-}>(C_6H_4 \cdot OAc)_2$, prepared by heating the imidophthaleïn with acetic anhydride, is obtained as a colourless, crystalline powder melting at 254—256°.

Tetrabromimidophenolphthaleïn is prepared by heating tetrabromophenolphthaleïn with ammonia or by brominating imidophenolphthaleïn; the former method was employed by Burkhardt (*loc. cit.*). It is obtained in minute, orthorhombic crystals melting and decomposing at about 310°. On treating its alcoholic solution with nitrous acid, a yellow crystalline substance was obtained which gave unsatisfactory numbers on analysis; the mother liquors seem to contain a dinitrobromophenol [OH : Br : (NO₂)₂ = 1 : 2 : 4 : 6 ?].

Triacetyltetrabromimidophenolphthaleïn,

$$CO<^{C_6H_4}_{NAc}>C(C_6H_2Br_2 \cdot OAc)_2,$$
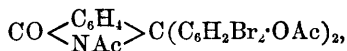
is prepared by boiling the above tetrabromo-derivative with acetic anhydride; it crystallises in colourless, birefringent octahedra melting at 176—178°, and dissolves in concentrated sulphuric acid yielding a characteristic violet solution.   W. J. P.

Naphthyl Iodochlorides and Moniodosonaphthalenes. By C. WILLGERODT (*Ber.*, **27**, 590—593).—The *naphthylic iodochlorides*, $C_{10}H_7 \cdot ICl_2$, were prepared by passing chlorine into cooled chloroform or acetic acid solutions of the iodonaphthalenes. The α-compound is an orange, apparently amorphous, very unstable substance, and decomposes at 30—45° when heated. The β-isomeride forms yellow needles, and decomposes at 56—61°. When these compounds are shaken with excess of dilute aqueous soda, they are converted into the corresponding *iodosonaphthalenes*, $C_{10}H_{17} \cdot IO$. Of these the α-compound, which was not obtained quite pure, was amorphous, yellowish-grey in colour, perfectly stable at the ordinary temperature, and decomposed when heated to 85—125°. The β-isomeride is an amorphous, yellowish-grey substance, and decomposes noiselessly at 127—128°.   C. F. B.

Isomerism of Diazo-compounds. By E. BAMBERGER (*Ber.*, **27**, 679—684).—β-Diazonaphthalene, on oxidation with potassium ferricyanide in alkaline solution, yields the following three compounds :—

Naphthalene-2 : 1-diazoxide, $C_{10}H_6<^N_O>N$, crystallising in golden yellow needles, or large quadratic plates, and melting at 76°; *β-naphthalenediazoic acid*, $C_{10}H_7 \cdot NH \cdot NO_2$, crystallising in colourless, highly lustrous needles, which melt at 131·5—136°, according to the rapidity of heating; *β-isodiazonaphthalene* (*β-naphthylnitrosamine*), $C_{10}H_7 \cdot NH \cdot NO$, which is deposited in crystalline flocks, consisting of

slender, colourless needles. The relative quantity in which these substances are formed depends on the experimental conditions; β-isodiazonaphthalene is obtained by the action of concentrated soda on β-diazonaphthalene; it is a tolerably strong acid, and is distinguished from the isomeric β-diazonaphthalene by its sparing solubility, its inability to combine with phenols in alkaline solution to form azo-dyes, and the stability of its alkaline solution. In presence of acids, the compound is rapidly converted into diazonaphthalene, it is very unstable at ordinary temperatures, and has therefore not been analysed. By the action of potassium ferricyanide, β-iso liazonaphthalene is readily converted into β-naphthalenediazoic acid (see above). With methylic iodide, β-naphthylmethylnitrosamine, $C_{10}H_7 \cdot NMe \cdot NO$, is formed, and crystallises in colourless, lustrous, feathery needles, melting at 86°, it is readily volatile with steam, and gives the Liebermann reaction. The *sodium salt* crystallises from dilute soda in silvery, lustrous plates: it decomposes on heating; in aqueous solution it is somewhat unstable, and on boiling, nitrogen is evolved, and the solution becomes red. The *barium, lead, zinc,* and *silver salts* are colourless, crystalline, and sparingly soluble, the last explodes on heating.

The following compounds are formed by the action of potassium ferricyanide on α-diazonaphthalene in alkaline solution:—*azonaphthalene*, $C_{10}H_7 \cdot N:N \cdot C_{10}H_7$; α-naphthylamine; *naphthalenediazoic acid,* $C_{10}H_7 \cdot NH \cdot NO_2$, crystallising in golden, yellow-bronze, lustrous plates or needles, and melting at 118°; *naphthalene*-1 : 2-*diazoxide,*

$$C_{10}H_6 < ^N_O > N,$$
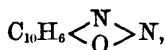
crystallising in thick, amber-coloured, lustrous plates, melts at 95°. The last compound, on reduction, is converted into ammonia, and α-amido-β-naphthol, from which it is regenerated by means of the diazo-reaction.

α-Isodiazonaphthalene (α-naphthylnitrosamine) is prepared like the β-derivative, which it closely resembles, by the action of soda on α-diazonaphthalene; it is stable in alkaline solution, but in presence of acids is quickly converted into diazonaphthalene.

Paradiazosulphanilic acid, like the diazonaphthalenes, also yields an isomeric compound by the action of soda; in presence of acids, the reverse change takes place; the reaction is being further investigated. The interaction of silver diazobenzene and methylic iodide at 0° has also been partially studied, a considerable number of products are formed, the chief being iodobenzene.   J. B. T.

Nitro-β-naphthaquinone. By T. ZINCKE and O. NEUMANN (*Annalen,* **278,** 173—207).—When finely-powdered nitro-β-naphthaquinone is dissolved by warming in methylic alcohol, and the solution allowed to remain in the cold, a compound, $C_{12}H_{13}NO_6$, is obtained, which, when pure forms colourless crystals, and melts at 143°, with darkening and evolution of gas; it dissolves readily in hot absolute alcohol and other solvents, but the crystals which separate on cooling are yellowish. The constitutional formula

$C_6H_4 \cdot CO- C(OH) \cdot OMe$
$CH(OMe) \cdot C:NO \cdot OH$,(α-methoxy-β-nitrodiketohydronaphthalene meth-oxide), explains its reactions. Cold sulphuric and nitric acid or hot acetic acid decompose the compound, regenerating nitro-β-naphthaquinone, whilst the products of the actions of alkalis appear to be the same as those from β-nitronaphthaquinone.

When the last-described compound is dissolved in a solution of bleaching powder, a mixture of orthodichloronitromethoxyethylbenzoyl-carboxylic acid, $NO_2 \cdot CCl_2 \cdot CH(OMe) \cdot C_6H_4 \cdot CO \cdot COOH$, and its methylic salt is obtained. The acid crystallises from a mixture of light petroleum and benzene in transparent tables, and melts at 116°; the methylic salt melts at 90°. When the acid is heated with acetic chloride in a sealed tube at 120—130°, it yields the lactone
$CO \cdot O$
C_6H_4 $>CH \cdot CCl_2 \cdot NO_2$, which, if heated with potassium acetate, gives dichloromethylenephthalide (compare Zincke and Latten, Abstr., 1892, 1231).

If the acid just described is treated with chromic acid or bleaching powder solution, orthodichloronitromethoxyethylbenzoic acid, $NO_2 \cdot CCl_2 \cdot CH(OMe) \cdot C_6H_4 \cdot COOH$, is obtained; this melts at 187°, and its methylic salt at 89° (compare also loc. cit.). The lactone mentioned above is formed when the acid is heated with sulphuric acid or acetic chloride.

Orthodichloronitromethoxyethylbenzoic acid and the lactone obtained from it (see above) both yield homophthalic acid when heated with hydriodic acid and phosphorus in a sealed tube at 160—180°.

The compound, $\begin{array}{l}C_6H_4 \cdot CO—C(OMe) \cdot OH, \\ CH(OMe) \cdot CCl \cdot NO_2\end{array}$ is formed by passing chlorine into a solution of α-methoxy-β-nitro-diketohydronaphthalene methoxide in chloroform; it crystallises in lustrous needles, melts between 117° and 123°, and, when heated with acetic chloride, yields the dihydroxy-derivative, $\begin{array}{l}C_6H_4 \cdot CO—C(OH)_2, \\ CH(OMe) \cdot CCl \cdot NO_2\end{array}$ which melts at 137°; the chlorinated methoxide is regenerated from the latter by treatment with methylic alcohol. Orthochloronitromethoxyethylbenzoylcarb-oxylic acid, $OH \cdot NO:CCl \cdot CH(OMe) \cdot C_6H_4 \cdot CO \cdot COOH$, is obtained by treating the chlorinated methoxide with alkali; it forms small, colourless crystals, and melts at 189°. The methylic salt melts at 100°; the acetyl derivative, $C_{11}H_9ClAcNO_6$, obtained by the action of acetic chloride on the acid at 120—130°, is an indifferent compound melting at 179°; the acetyl derivative of the methylic salt melts at 115°. When orthochloronitromethoxyethylbenzoylcarboxylic acid is treated with bleaching powder solution, dichloromethoxyethylbenzoic acid (see above) is formed; whilst by the action of chromic acid orthochloromethoxyethylbenzoic acid (Zincke and Latten loc. cit.) is obtained. A. R. L.

Orientation in the Terpene Series. By A. v. BAEYER (Ber., **27**, 810—816; compare this vol., i, 92 and 252).—Hydrobromocarvole, $C_{10}H_{14}O,HBr$, has been previously obtained by Goldschmidt and

Kisser (Abstr., 1887, 923), by the action of hydrogen bromide on carvole, and is prepared by the action of hydrogen bromide in glacial acetic acid solution on carvole, at low temperatures; it is deposited from ether in camphor-like, crystalline masses, has no smell, and melts at 32°. Part of the substance melts at a lower temperature; it is identical with hydrobromocarvole in its chemical properties, and the reason for the difference in melting point has not yet been determined. Hydrobromocarvoxime is formed by the action of hydroxylamine on the preceding compound, and melts at 136°, instead of 116° as stated by Goldschmidt and Kisser, who obtained it by treating carvoxime with hydrogen bromide in methylic alcoholic solution (*loc. cit.*).

The action of methylic alcoholic potash (1 : 2) at low temperatures on hydrobromocarvole converts it into *eucarvole*, $C_{10}H_{14}O$, not into carvole, as Goldschmidt and Kisser found; this boils at 210—215°, and is partially decomposed into carvacrole; under 25 mm. pressure it boils at 104—105°, without decomposition; the sp. gr. = 0·948 at 20°/4°; it is optically inactive, and is quantitatively converted into carvacrole by heating for an hour at its boiling point. Eucarvole does not combine with sodium hydrogen sulphite; it derives its name from the production of a pure, deep blue colour on heating with methylic alcoholic potash; the colour is unstable, and disappears on the addition of water. The *phenylhydrazone* is oily; the *oxime* is indistinguishable from carvoxime in appearance, and melts at 106°. The following reactions show the difference between eucarvoxime, carvoxime, and isocarvoxime. (1.) By boiling with dilute sulphuric acid, carvoxime and isocarvoxime are immediately converted into carvole and carvacrole respectively; eucarvoxime is much more stable. (2.) Concentrated sulphuric acid acts on carvoxime and isocarvoxime, with development of heat and formation of crystalline compounds, which have not yet been investigated. Eucarvoxime dissolves without change. (3.) Bechmann's chromic acid mixture colours crystals of carvoxime black; crystals of isocarvoxime and eucarvoxime are not blackened. (4.) Ferric chloride in alcoholic solution gives a green coloration with eucarvoxime, and a yellow colour with carvoxime and isocarvoxime. (5.) Boiling methylic alcoholic potash is without action on carvoxime or eucarvoxime; isocarvoxime is decomposed into an oily liquid. (6.) Bromine yields apparently different crystalline compounds with all three oximes. On the assumption of the absence of the semicyclic double linkage [4,8], the following formulæ represent the three carvoles,

$$CMe{<}^{CO\cdot CH}_{CH\cdot CH_2}{>}CPr; \quad CMe{<}^{CO\cdot CH_2}_{CH\cdot CH}{>}CPr;$$

Carvole.   Eucarvole.

$$CHMe{<}^{CO\cdot CH}_{CH:CH}{>}CPr;$$
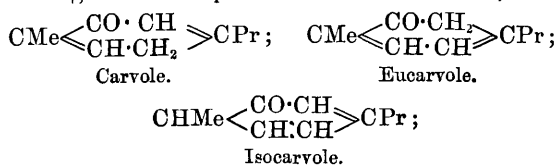
Isocarvole.

isocarvole must be tautomeric with carvacrole, or converted into it with the greatest ease, as shown by the action of dilute sulphuric acid on the oxime; eucarvole is converted into carvacrole at its boiling point,.

whilst carvole only yields carvacrole with difficulty. Eucarvole on reduction with sodium and alcohol, yields an isomeric dihydro-carveol boiling at 217—219° (corr.), and resembling menthol in odour. On oxidation with chromic acid mixture, a compound is obtained which smells of camphor, combines with hydroxylamine, but not with sodium hydrogen sulphite, and is being further investigated. Hydrobromocarvolephenylhydrazone melts at 123—124°, and carvolephenylhydrazone at 109—110°, instead of 119° and 106° respectively, as stated by Goldschmidt and Kisser.

In continuation of his past paper on terpinene, the author states that $\Delta^{4(8)}$-terpen-1-ol is formed in considerable quantity in the preparation of terpinol from terpin and oxalic acid or phosphoric anhydride; it boils at 69—70°, not at 69—90°, as stated, and is isolated by means of the blue nitrosochloride; Schimmel's liquid terpenol, under similar circumstances, does not yield any blue compound. The presence of terpinene in other terpentine oils can be detected by the production of a brown colour, or of brown flocks, on shaking with the following mixture:—Sodium dichromate (6 parts), concentrated sulphuric acid (5 parts), water (30 parts); as this is without action on the other constituents of terpentine oils, the terpinene is readily eliminated by repeated treatment with the oxidising mixture at ordinary temperatures. J. B. T.

Quercitrin and Allied Compounds. By R. WACHS (*Chem. Centr.*, 1894, i, 50—51; from *Pharm. Post.*, **26**, 529—530).—The substances investigated were quercitrin from quercitron bark; yellow colouring matters from the flower buds of *Sophora japonica;* similar substances from *Viola tricolor var. vulg.*, from the leaves of *Aesculus hippocastanum*, from those of *Thuja occidentalis*, and from the flower buds of *Capparis spinosa*. These substances are divisible into two classes, the one includes quercitrin and chestnut-quercitrin, the other contains the remainder, with the exception of thujin, which occupies an intermediate position, but its derivative thujetin differs considerably from quercetin. Quercitrin, $C_{21}H_{20}O_{11}$, contains $1H_2O$ less than chestnut-quercetin, $C_{21}H_{22}O_{12}$; the members of the second group have the formula $C_{27}H_{30}O_{16}$; on hydrolysis, the members of both groups yield compounds of the formula $C_{15}H_{10}O_7$, which are identical or isomeric with quercetin, but caper-quercetin appears to be $C_{15}H_{12}O_7$. The compounds from *Viola tricolor*, *Sophora*, *Capparis spinosa*, and *Thuja*, yield glucose on hydrolysis, in addition to isodulcitol. The amount of sugar formed on hydrolysis varies considerably, as shown in the following table.

	Sugar as isodulcite, per cent.	Quercetin, per cent.
Quercitrin	38·99	68·65
Sophorin	57·16	49·54 (sophoretin)
Viola-quercitrin	55·78	51·86
Chestnut-quercitrin	36·83	65·65
Caper-quercitrin	56·73	49·61
Thujin	38·16	62·25 (Thujetin)

J. B. T.

New Constituent of True Coto Bark. By G. CIAMICIAN and P. SILBER (*Ber.*, **27**, 841—850).—The substance which forms the subject of this paper was obtained in the purification of cotoïn on the large scale. It forms yellowish crystals melting at 66—68°, and has the formula $C_{11}H_8O_2$. In chemical properties, it is closely allied to paracotoïn, which the authors consider to be dioxymethylene-phenylcoumalin, but differs from it by the absence of the dioxy-methylene group, so that it receives the name (provisionally) of *phenylcoumalin*. It may be purified by treatment with hydrobromic acid, which forms an unstable compound with it, and this decomposes gradually, leaving the original substance, which then only requires to be freed from acid by dissolving it in alcohol and precipitating with water. It is readily soluble in ether, alcohol, acetic acid, &c., but only very sparingly in water. It dissolves in alkalis and alkali carbonates, yellow solutions being formed, which smell of acetophenone. Sulphuric acid in the cold dissolves the compound without alteration. It is, moreover, not acted on by acetic anhydride or hydriodic acid, and therefore does not contain hydroxyl- or methoxyl-groups. *Bromophenylcoumalin*, $C_{11}H_7BrO_2$, is produced by the action of bromine on a solution of the substance in chloroform, and forms yellowish crystals melting at 138—139°.

Nitric acid converts the original compound into a *mononitro-derivative*, which forms rhombic tablets melting at 161°. Like paracotoïn, the new substance reacts with phenylhydrazine, and yields a compound of the formula $C_{23}H_{22}N_4O$, which crystallises in slender, white needles, and melts at 198°. It also reacts with aniline, forming a compound which crystallises in needles, and melts at 143°.

When boiled with aqueous alkalis, phenylcoumalin yields acetophenone, and an amorphous acid which could not be obtained crystalline. When fused with potash, it gives benzoic acid, thus corresponding closely with paracotoïn. When it is heated with hydrochloric acid at 140°, phenylcoumalin is converted into a white, crystalline product which melts at 214°, and has the same composition as the original substance, of which it is probably a polymeride.

When heated with methylic iodide and alcoholic potash, phenyl-coumalin is converted into a *dimethyl-derivative*, which crystallises in long, yellowish needles, melting at 100—101°. This compound corresponds with the dimethyl-derivative of paracotoïn, and is decomposed by alkalis, with formation of ethylphenyl ketone.

The properties of this new substance, and of paracotoïn itself, are, as already explained, best accounted for on the supposition that these substances are coumalin derivatives of the formulæ

$$CPh<^{CH \cdot CH}_{O-CO}>CH \quad \text{and} \quad CH_2<^O_O>C_6H_3 \cdot C<^{CH \cdot CH}_{O-CO}>CH.$$
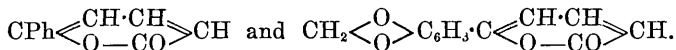
They cannot, however, like the other known coumalin-derivatives, be readily converted into compounds of the pyridine series, or into the ether of the corresponding hydroxy-acid. On the other hand, di-methylcoumalin (mesitene lactone) is converted by the action of methylic iodide and potash into a trimethyl-compound, and thus resembles both the substances under discussion. The *trimethylcou-*

malin thus formed separates from water in long white needles containing $3H_2O$, and melting at 45—46°. The anhydrous substance melts at 74°.

It is not impossible that the substance described by Jobst and Hesse as dicotoïn may prove to be impure phenylcoumalin.

A. H.

Kamala and Rottlerin. By P. BARTOLOTTI (*Gazzetta*, **24**, i, 1—7). —The author confirms the formula $C_{11}H_{10}O_3$, previously assigned to rottlerin, but has evidently overlooked the paper, published some months previously to his own, by A. G. Perkin (Trans., 1893, 975). The author finds that rottlerin melts at 200—201°, whilst Perkin gives the melting point as 191—191·5°. The so-called "kamaline," put into the market by Merck, of Darmstadt, is simply rottlerin.

Dibenzoylrottlerin, $C_{11}H_8Bz_2O_3$, and *rottlerin hydrazone,*

$$C_{11}H_{10}O_2 \cdot N_2HPh,$$
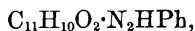
are yellow powders, which decompose on heating, and are soluble in the ordinary solvents.

The ash of kamala contains a considerable proportion of manganese.

W. J. P.

Amidopyridinecarboxylic acid. By A. PHILIPS (*Ber.*, **27**, 839—840).—When ammonia is passed into a solution of quinolinic acid in benzene, the *ammonium quinolinaminate,*

$$NH_2 \cdot CO \cdot C_5NH_3 \cdot COONH_4,$$

is formed. When heated for some time at 120—130°, this substance passes into quinolinic imide, $C_5NH_3{<}^{CO}_{CO}{>}NH$, which melts at 230°, and readily combines with ammonia, forming the *diamide* of *quinolinic acid,* $C_5NH_3(CONH_2)_2$. The free *quinolinaminic acid,*

$$NH_2 \cdot CO \cdot C_5NH_3 \cdot COOH \ [= 2 : 3],$$
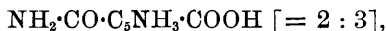
is obtained by passing sulphurous anhydride into an aqueous solution of the ammonium salt, and forms white needles melting at 168°, with evolution of gas. When its aqueous solution is heated, it combines with water to produce ammonium hydrogen quinoliuate. Quinolinaminic acid, when treated with sodium hypobromite, is readily converted into 2 : 3-*amidopyridinecarboxylic acid*, $NH_2 \cdot C_5NH_3 \cdot COOH$, which forms white needles, melting with evolution of gas at 210°. When heated, this compound loses carbonic anhydride, and yields α-(2)-amidopyridine identical with that described by Marckwald (Abstr., 1893, i, 727). Quinolinaminic acid and the amidopyridinecarboxylic acid derived from it, have therefore the constitutions given above.

A. H.

Oxidation of Reduced Quinolines. By J. TAFEL (*Ber.*, **27**, 824—826).—3-Methyltetrahydroquinoline, 1-methyltetrahydroquinoline, and tetrahydroquinaldine are oxidised by treatment with mercuric acetate in the manner previously described (Abstr., 1892, 1104); the yield varies from about 40 to 60 per cent. of the theoretical.

Tetrahydroquinoline-1-carboxylic acid, $COOH \cdot C_6H_3 {<}^{CH_2 \cdot CH_2}_{NH \cdot CH_2},$ is prepared by the reduction of orthoquinolinecarboxylic acid with tin and hydrochloric acid, and crystallises in colourless needles melting at 163° (uncorr.), and subliming at higher temperatures. In neutral or alkaline solutions it exhibits a blue fluorescence; with dilute sulphuric acid and oxidising agents in aqueous solution, a brownish-red precipitate is produced. On oxidation with mercuric acetate, 1-quinolinecarboxylic acid is only formed in small quantity, the larger portion being decomposed into tetrahydroquinoline and carbonic anhydride. Attempts to prepare hydroxyquinoline or methoxyquinoline from the tetrahydroderivatives, have led to negative results. J. B. T.

Allylamidothiazoles and their Isomerides. By G. MARCHESINI (*Gazzetta*, **24**, i, 65—70; compare this vol., i, 209).—2 : 5-*Methyl-dibenzylamidothiazole,* ${}^{CH - S}_{CMe \cdot N}{>}C \cdot N(C_7H_7)_2,$ is prepared by heating unsymmetrical dibenzylthiocarbamide with chloracetone in alcoholic solution in a reflux apparatus; it crystallises in long, yellowish needles melting at 50°, and is soluble in alcohol or ether. It is precipitated unaltered from its alcoholic solution, and gives no precipitate with alcoholic silver nitrate.

1 : 2 : 5-*Benzylmethylbenzylimidothiazoline hydrochloride,*

$$\begin{matrix} CH \rule{1cm}{0.4pt} S \\ \| \qquad\quad {>}C{:}N \cdot C_7H_7, HCl, \\ CMe \cdot N(C_7H_7) \end{matrix}$$
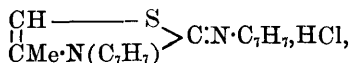
is prepared by heating symmetrical dibenzylthiocarbamide and chloracetone in alcoholic solution; it crystallises in small, white scales, and melts at 194°. The *hydrobromide* is obtained in small, white laminæ, melting at 198°, and is very soluble in alcohol.

The product obtained by heating benzylic iodide with 2-phenylamidothiazole at 150°, in an oil bath, contains a *substance* having the composition of 1 : 2 : 5-benzylphenylbenzylimidothiazoline; it forms white crystals melting at 138°, and is soluble in alcohol or ether. A small proportion of a *substance* melting at 128° accompanies it. W. J. P.

Pyrazole Compounds. By L. BALBIANO and G. MARCHETTI (*Gazzetta*, **24**, i, 8—14; compare Abstr., 1893, i, 672).—*Dibenzoyl-3 : 5-dimethylpyrazole* is obtained by heating 3 : 5-dimethylpyrazole with benzoic chloride at 250—260°; it crystallises in small, white prisms melting at 124—124·5°, and is soluble in ether or hot alcohol. On warming with sodium ethoxide in alcoholic solution, it yields *4-benzoyl-3 : 5-dimethylpyrazole,* $NH {<}^{CMe{:}CBz}_{N = CMe};$ this crystallises in lustrous, white needles, which contain $2H_2O$, and melts at 59—60°. It is soluble in alcohol or ether, and is not attacked by alcoholic potash. On treating its solution in aqueous alcoholic potash with ammoniacal silver nitrate solution, the *argento*-derivative, $C_3N_2Me_2BrAg$, separates as a caseous mass.

4-Benzoyl-1 : 3 : 5-*triphenylpyrazole* is prepared by heating 1 : 3 : 5-triphenylpyrazole with benzoic chloride at 250—260° ; it crystallises in yellowish, lustrous needles melting at 172—173°, and is sparingly soluble in alcohol or ether. It is not attacked by alcoholic potash. No benzoyl-derivative of 1 : 4 : 5-phenylmethylethylpyrazole could be obtained. Attempts to prepare a trimethylenediamine isomeric with cadaverine by reducing 3 : 5-dimethylpyrazole with tin and hydro-chloric acid also failed. W. J. P.

Oxazines and Eurhodines. By C. LAUTH (*Compt. rend.*, **118**, 473—476).—Nitrosodimethylaniline was reduced with zinc and hydrochloric acid, and then treated with sodium thiosulphate, hydrogen carbonate, and carbonate. The mercaptan thus obtained was mixed with an acid solution of diethylamidophenol, and the mixture oxidised with potassium dichromate, and neutralised with sodium carbonate. The dark blue solution was boiled, and the precipitate collected, washed, dissolved in dilute hydrochloric acid, precipitated with sodium chloride, redissolved in sodium carbonate solution, and precipitated with zinc and sodium chlorides, and finally crystallised from alcohol.

The blue-violet colouring matter thus obtained is somewhat soluble in water and alcohol, very slightly soluble in sodium carbonate solution, more soluble in ammonia. Ether removes only traces from the ammoniacal solution. It dissolves in concentrated sulphuric acid, forming a red-violet solution, and in concentrated hydrochloric acid, forming an olive-green solution. Dilute acids form pure blue solutions. The colouring matter dyes silk, wool, and cotton mordanted with tannin, a violet-blue. It contains no sulphur, and must be regarded as an oxazine of the constitution

$$NMe_2Cl < \begin{matrix} N{-\!\!-\!\!-}C_6H_3 \cdot NMe_2 \\ | \qquad\qquad | \\ C_6H_3 \cdot O \end{matrix}.$$
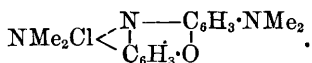
Direct oxidation of a mixture of amidodimethylaniline and diethylamidophenol yields a blue compound which, however, is very different from the oxazine, and has the properties of an indamine. It is very soluble in alkalis, is completely decomposed by acids and by boiling with water, and when boiled with aniline acetate in presence of a dichromate it yields a safranine. It may be regarded as having the constitution $NMe_2Cl < \begin{matrix} N \cdot C_6H_3(OH) \cdot NMe_2 \\ | \\ C_6H_4 \end{matrix}$. The author did not succeed in converting this indamine into the oxazine, but its formation indicates that when the mixture of mercaptan and diethylamidophenol is oxidised, there is first formed a sulphonated thioindamine, and when this is boiled with water in presence of an oxidising agent, the S·SO₃H group is eliminated, and the oxygen of the hydroxyl is fixed on the two nuclei in a manner analogous to the formation of methylene-blue.

The compound described is different from that obtained by the action of nitrosodimethylaniline on diethylamidophenol, but, in view of the irregular behaviour of nitrosodimethylaniline, the latter reac-

tion cannot be regarded as evidence against the formation of an oxazine. Moreover, when equal molecular proportions of metamido-dimethylaniline and the sulphonated mercaptan of paramidodimethyl-aniline are oxidised, tetramethyleurhodine is formed by a reaction analogous to that which gives rise to an oxazine. C. H. B.

Derivatives of Thiosemicarbazides. By G. PULVERMACHER (*Ber.*, **27**, 613—630; compare this vol., i, 76).—Phenyl-, methyl-, and allyl-thiocarbimides, with hydrazine hydrate, in cooled alcoholic solution, yield thiosemicarbazides, $NHR \cdot CS \cdot NH \cdot NH_2$, and these, with aldehydes $R \cdot CHO$, form compounds $NHR \cdot CS \cdot NH \cdot N \cdot CHR$. With crystallisable formic acid, they yield formyl derivatives,

$$NHR \cdot CS \cdot NH \cdot NH \cdot CHO,$$

which, when boiled with acetic chloride, lose water, and yield bases,

$$NR \colon C <^{S-CH}_{NH \cdot N}$$; phenylthiosemicarbazide, however, yields the base

directly, without the intermediate formation of a formyl derivative. To these bases, the name of *alkylimidothiobiazolines* is given, in accordance with Freund's nomenclature (Abstr., 1890, 1440). They yield nitroso-derivatives, and, with acetic anhydride, acetyl-derivatives. When heated at 100° with methylic iodide, *n*-methyl-derivatives,

$$NR \colon C <^{S-CH}_{NMe \cdot N}$$, are formed which yield methylamine when decom-

posed by hydrochloric acid at 180°. Isomeric *c*-methyl-derivatives,

$$NR \colon C <^{S-CMe}_{NH \cdot N},$$
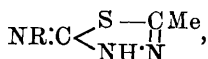
are obtained by·the action of acetic chloride on the thiosemicar-bazides; these also yield nitroso-, acetyl-, and *n*-methyl-derivatives,

the last being $NR \colon C <^{S-CMe}_{NMe \cdot N}$. These bases are very stable; they

are not affected when boiled with 15 per cent. hydrochloric acid or with caustic soda, or when reduced with tin and hydrochloric acid, nor does boiling with freshly precipitated mercuric oxide remove any sulphur from them.

Phenylthiosemicarbazide, which forms colourless, hexagonal prisms, and melts with decomposition at 140°, is decomposed by boiling with various reagents; with hydrochloric acid. it yields phenylthiocarba-mide; with soda, phenylcarbamide; with mercuric oxide, phenyl-carbamine and mercuric sulphide; with acetic acid, hydrogen sulphide and the base, $C_{14}H_{14}N_4S_2$, obtained by Freund and Wischewiansky (this vol., i, 98). Its *benzal-*, *salicylal-*, *cinnamylidene-*, and yellow *metanitrobenzal-derivatives* melt respectively at 191°, 183°, 175—176°, and 193—194°. *Phenylimidothiobiazoline* melts at 173°; the *hydro-chloride* contains 1HCl. The *nitroso-* and *acetyl-derivatives* melt at 80—81° and 142° respectively; the yellow *n-methyl-derivative* melts at 258°, its yellow *hydriodide* at 203—204°; the *c-methyl-derivative* at 193—194°, its *hydrochloride* ($\frac{1}{2}$HCl) at 190—191°, and its yellow *nitroso-* and colourless *acetyl- derivatives* at 114—115° and 148° respectively; the greenish *c∶n-dimethyl derivative* melts at 193—194°, its

hydriodide at 198°. The action of benzoic chloride on phenylthiosemi-carbazide is anomalous; two products are obtained melting at 281° and 200° respectively, neither of which are basic, one having even slightly acid properties.

Methylthiosemicarbazide melts at 137—138°, its *benzal derivative* at 160°, and its *formyl derivative* at 167—168°; the latter is decomposed into its components by boiling with aqueous soda. *Methyl-imidothiobiazoline* melts at 65—66°, the *hydrochloride* at 245°. The *hydriodide* of the *n-methyl derivative* melts at 232—233°; the *c-methyl derivative* at 112°, its *hydrochloride* at 211—212°, and *nitroso derivative* at 56°; the *c : n-dimethyl derivative* at 248—249°, its hydriodide at 150—151°.

Allylthiosemicarbazide melts at 98—99°; its *benzal-, salicylal-, cin-namylidene-,* and *metanitrobenzal-* derivatives respectively at 124—125°, 149—150°, 165—166°, and 163°; its *formyl- derivative* at 128—129°. *Allylimidothiobiazoline* melts at 73°; the *hydrochloride* at 128—130°, the *acetyl-derivative* at 57°. The *hydrochloride* of the *n-methyl deriva-tive* melts at 176—177°; the *c-methyl derivative* forms small plates, its *hydrochloride* melts at 172—173°, and its *acetyl derivative* at 77—78°; the *hydriodide* of the *c:n-dimethyl derivative* melts at 115—116°. With benzoic chloride, allylthiosemicarbazide yields a *benzoyl-derivative*, melting at 171°, and this, when heated with acetic chloride, is converted into *allylimido-c-phenylthio-biazoline,* which melts at 115°, its *hydrochloride* at 113°, and its *acetyl-* and *nitroso-derivatives* at 123—124° and 95° respectively. C. F. B.

Constitution of the Carbizines. By C. D. HARRIES and E. LOEWENSTEIN (*Ber.*, **27**, 861—868).—Diphenyldimethylthiocarb-azide, $CS(NH·NMePh)_2$, melts sharply at 176°, and not indefinitely at 168°, as stated by Stahel (*Annalen*, **258**, 242). *Diphenyldimethyl-thiosemicarbazide*, $NMePh·CS·NH·NMePh$, is obtained by heating a mixture of methylphenylhydrazine, methylaniline, and carbon bisulph-ide with alcohol on the water bath. It forms large, rhombic prisms melting at 113°, and is insoluble in light petroleum and in water. It is dissolved without alteration by hydrochloric acid, and is not decomposed by yellow mercuric oxide.

Phenylmethylthiosemicarbazide, $NMePh·NH·CS·NH_2$, is obtained from phenylmethylhydrazine sulphate and ammonium thiocyanate in alcoholic solution. It crystallises in microscopic octohedra, melts at 187°, and is slightly soluble in ether, almost insoluble in light petr-oleum and in benzene.

Phenylmethylthiocarbizine, $C_6H_4 <{\overset{NMe·N}{\underset{S——CH}{|}}}$, is prepared by boiling diphenyldimethylthiosemicarbazide with hydrochloric acid in dilute alcoholic solution, methylaniline being also formed. The *hydrochloride,* $C_8H_8N_2S·HCl$, crystallises in fine needles, and the platinochloride in yellow, microscopic needles, as does also the aurochloride. The *picrate* crystallises in groups of yellow needles, and melts and decomposes at 240°. The free base melts at 123°, and is in every respect iden-tical with the compound obtained by Fischer and Besthorn (*Annalen,* **212**, 316) by the action of methylic iodide on phenylthiocarbizine.

When it is boiled in alcoholic solution with methylic iodide, *phenyl-methylthiocarbizonium iodide*, $C_8H_8N_2SMeI$, is formed, and this crystallises in groups of light yellow needles melting with decomposition at 280°. *Bromophenylmethylthiocarbizine*, $C_8H_7BrN_2S$, is obtained by direct bromination, and melts at 106°, whilst the *hydrobromide* melts with decomposition at 250°.

On heating the base with nitric acid, a *dinitro-compound* is produced, which forms very sparingly soluble, orange-yellow needles melting at 250° with decomposition.

When phenylmethylthiocarbizine is fused with potash, it forms *orthomethylamidophenyl mercaptan*, soluble in acids and alkalis. This compound if kept, is converted into the corresponding *bisulphide*, $S_2(C_6H_4·NHMe)_2$, which forms odourless, four-sided, golden-yellow tablets melting at 67—68°, and is reconverted by zinc-dust and dilute sulphuric acid into the mercaptan. Phenylthiocarbizine undergoes a similar decomposition when fused with potash, ortho-amidophenyl mercaptan being produced, but the decomposition does not take place so readily as with the methyl-derivative. This reaction renders it probable that in the formation of carbizine-derivatives from the thiosemicarbazides, the sulphur atom enters the benzene ring and forms part of a new six-atom ring. The formula thus obtained,

$C_6H_4 \begin{smallmatrix} NH·N \\ S—CH \end{smallmatrix}$, also agrees with the formation of phenylmethylthio-carbizine from diphenylmethylthiosemicarbazide, in which the phenyl- and methyl-groups are combined with the same nitrogen atom,

whereas the formula proposed by Fischer and Besthorn, $NPh \begin{smallmatrix} NH \\ CS \end{smallmatrix}$

is inconsistent with both of these facts.

Diphenylmethylethylthiosemicarbazide, $NEtPh·CS·NH·NMePh$, is prepared in a similar manner to the dimethyl derivative. It is very soluble in the usual solvents, crystallises in colourless plates, and melts at 83—84°. The corresponding *carbazide* melts at 176°.

Phenylmethylhydrazine also reacts with aniline in a similar manner. The substance formed appears to be identical with the compound melting at 154° described by Fischer.   A. H.

Isopipecoline and the Asymmetric Nitrogen Atom. By A. LADENBURG (*Ber.*, **27**, 853—858).—Coniine exists in four modifications (Abstr., 1893, i, 442), and the author has proposed to account for the fourth of these, isoconiine, by a theory involving the existence of an asymmetric nitrogen atom. Attempts to obtain evidence on this point by splitting up nitrogen derivatives into optically active isomerides have been made, but without success. Tetrahydroquinoline and tetrahydroisoquinoline were converted into the tartrates, but no different modifications could be obtained by the fractional crystallisation of these. *Tetrahydrisoquinoline hydrogen tartrate* melts at 140—142° and forms hemihedral rhombic crystals. The axial ratio of these is 0·95008 : 1 : 1·80913, and the principal angles (110) : (1$\bar{1}$0) = 87° 4′ ; (001) : (101) = 60° 56′.

d-*α*-Pipecoline hydrochloride, when it is distilled over zinc-dust, also yields a base possessing a lower rotatory power, and to this has

been given the name of isopipecoline. That this is a definite isomeride of α-pipecoline and not simply a mixture of the dextro- with a little of the lævo-variety, formed during the distillation, is proved by the fact that the hydrogen tartrate of this base solidifies completely on crystallisation, whereas that of r-pipecoline always leaves a certain amount of uncrystallisable syrup behind. An examination of the base prepared from the last fraction of isopipecoline hydrogen tartrate, moreover, proved that it had a much greater rotatory power than would have been the case if the original base had consisted of a mixture of the d-base with the r-base. The existence of isopipecoline may, therefore, be considered to be definitely established.

Another method proposed by the author to distinguish between an optical isomeride of less rotatory power and a mixture of an optically active base with a portion of the inactive modification of the same base, consists in converting the pure active form into some other active derivative, and thus obtaining the ratio of the rotations of these two. The substance to be tested is then similarly treated. If it be a mixture of the optically active with the inactive form, the same ratio should be obtained in the second case as in the first, provided the proportions of the active and inactive forms are not changed by the reaction. An experiment of this kind, carried out with isopipecoline, gave an indecisive result, the difference between the two ratios being almost within the limit of error, which was found to be about 8 per cent.

dv-*Methyl-α-pipecoline*, which was employed in this experiment, boils at 128—131°, and has a specific gravity of 0·825 at 16° and a rotatory power, $[\alpha]_D = +64\cdot99°$. A. H.

Pure d-Coniine. By A. LADENBURG (*Ber.*, **27**, 858—859).—Pure coniine boils at 166—167° and has a specific rotation equal to $[\alpha]_D = +15\cdot6°$. This number is identical with that given by Schiff (*Annalen*, **166**, 94), which has been mistaken by Landolt for the angle of rotation and used by him for the calculation of the specific rotation. The platinochloride of this substance is completely soluble in a mixture of alcohol and ether. When its alcoholic or aqueous solution is evaporated, it solidifies at once on cooling, whereas the platinochloride of the impure material generally remains oily for some time.

A. H.

Crystalline Form of Isoconiine Platinochloride. By A. LADENBURG (*Ber.*, **27**, 859—861).—This salt is dimorphous.

The form melting at 175° crystallises in the rhombic system, the axial ratio being 0·6971 : 1 : 0·38145 and the principal angles (120) : (010) = 35° 39' ; (101) : ($\bar{1}$01) = 57° 22·5'. The crystals are of two types, both being columnar, one type parallel to the vertical axis, the other parallel to the macrodiagonal.

The second form, melting at 160°, crystallises in monosymmetric tablets, the constants of which are :—Axial ratio, 1·3919 : 1 : 1·0570. Axial angle, 64° 30'. Principal angles :—(110) : (100) = 51° 29' ; (110) : (001) = 74° 27' ; (11$\bar{1}$) : (00$\bar{1}$) = 60° 11'. A.H.

Isoconiine and Asymmetric Nitrogen. By L. SIMON (*Bull. Soc. Chim.*, [3], **9**, 949—952).—A rejoinder to Ladenburg (this vol.,

i, 213). It is true that stereoisomerism is not possible in piperidine itself, but it can certainly occur in disubstituted piperidines of the type represented by the formula $CH_2 <^{CH_2 \cdot CR_2}_{CH_2 \cdot CH_2}> NH$. The cyclic arrangement of such a ring changes as it is viewed from one side or the other, and if the third bond of the nitrogen atom is not in the plane of the ring, there will be two different stereometric configurations accordingly as it lies on the one side or the other of the plane. If, however, the bond is in the plane of the ring, there will be no such isomerism. Ladenburg's failure to isolate isomerides of the hydroquinolines seems to show that the latter is the case.

The same reasoning applies to monosubstituted piperidines such as the coniines. If the third nitrogen bond is not in the plane of the ring, dextro- and lævo-coniine will each yield two isomerides, in the formula of one of which the bond is on the same side of the ring as the propyl-group, in that of the other, on the opposite side—Ladenburg's isoconiine is one of these isomerides.

Asymmetric nitrogen may serve, therefore, to modify the rotatory power due to asymmetric carbon, but cannot alone cause the rotation.

Jn. W.

Aconitine. By W. R. Dunstan (*Ber.*, **27**, 664).—A reply to Freund and Beck (see note, this vol., i, 263).

Aconitine. By M. Freund and P. Beck (*Ber.*, **27**, 720—733; compare this vol., i, 263).—This paper consists in the main of an amplification of that above referred to, the details of the experimental work being given in full.

Apoaconitine appears not to exist, and the so-called japaconitine, $C_{66}H_{86}O_{21}N_2$, is also identical with ordinary aconitine. The molecular weight of the latter in benzene solution was found to be 663 (calc. 645). The melting point of aconitine varies according to the rate at which it is heated. It is usually stated to be 188—189°, but when the temperature is rapidly raised, it is observed to be 197—198°. The α- and β-aurochlorides, the nitrate, and the hydrobromide all give numbers on analysis which agree well with the formula proposed by the authors (*loc. cit.*).

Picraconitine (isaconitine) aurochloride is amorphous, and melts indefinitely at 125—135°. The colourless compound melting at 204°, obtained by Dunstan and Harrison by the gradual evaporation of its alcoholic solution, could not be obtained. The hydriodide forms splendid white crystals which soften at 201—202°, and then melt at 204—205°. The hydriodide of isaconitine melts, according to Dunstan, at 246°. *Picraconitine nitrate* is only slightly soluble in water, and crystallises from alcohol in coarse prisms, which become yellow at 210°, and decompose at 240—250°.

The second crop of crystals from the liquid obtained by boiling aconitine with water consists of the acetate of picraconitine. The mother liquor, after the removal of all the picraconitine, yielded, after neutralisation and evaporation, a residue of aconine, which was converted into the hydrochloride. This substance agrees in proper-

ties with the compound described by Dunstan and Passmore, but appears from a number of analyses to have the formula

$$C_{25}H_{41}NO_9,HCl,$$

and not $C_{26}H_{41}NO_{11},HCl,2H_2O$, which has been ascribed to it.

Aconine is also formed by the action of boiling alcoholic potash on picraconitine.

When picraconitine is boiled with acetic anhydride, it yields, along with an amorphous substance, an *acetyl-derivative*, $C_{32}H_{44}AcNO_{10}$, which crystallises from alcohol in prisms melting at 255—256°.

Aconine and picraconitine contain the four methylic groups originally present in the molecule of aconitine. A. H.

Ptomaïne from Damaged Cheese. By C. LEPIERRE (*Compt. rend.*, **118**, 476—478).—1 kilo. of a ripe cheese from ewes' milk, which gave rise to digestive troubles when eaten, was found to be free from metallic poisons, and yielded no poisonous proteïd or albumose, but when treated by Gautier's process, it gave some decigrams of a well crystallised base of the composition $C_{16}H_{24}N_2O_4$. It has no odour, but a bitter taste, is slightly acid to phenolphthaleïn, dissolves very slightly in water, but is soluble in alcohol, and yields a *hydrochloride*, which is very soluble and crystallises in large needles. The *platinochloride* and the *aurochloride* are also crystallisable. The specific rotatory power of the base is $[\alpha]_D = +11\cdot3°$ in aqueous solution. Its salts are precipitated by acid sodium phosphomolybdate, picric acid, and solution of iodine in potassium iodide, but not by tannin.

When administered by ingestion to a guinea pig, the base produced diarrhœa; but an aqueous solution of the hydrochloride, when injected into the vein of a rabbit's ear, produced no ill effects.

No other definite bases were isolated, but the bases not precipitated by cupric acetate yielded small quantities of pyrroline when distilled with barium hydroxide.

Other cheeses of the same kind and age yielded no similar base.

C. H. B.

Crystallisation of Egg-albumin. By S. BONDZYŃSKI and L. ZOJA (*Zeit. physiol. Chem.*, **19**, 1—18).—Elementary analysis of egg-albumin has, in the hands of different observers, yielded different results. This appears to be in part owing to the fact that sometimes the globulin in egg-white has not been previously separated from the albumin. But in those cases where the albumin itself has been analysed, discordant results have suggested that egg-albumin is not a single substance but a mixture of albumins. In the present research, facts were discovered which bear out this supposition; the method adopted was that of Hofmeister.

Large quantities of egg-white were half saturated with ammonium sulphate, and after the globulin thus precipitated had been removed by filtration the albumin slowly crystallised out from the filtrate. The fractional method of crystallisation was adopted, and the different fractions examined; they were found to differ in their properties

(solubilities, temperature of heat coagulation, and specific rotation) and slightly in elementary composition.

Attempts to crystallise egg-globulin, and the proteïds of serum, led to negative results.   W. D. H.

Caseïns and Fibrins. By M. ARTHUS (*J. Pharm.*, **29**, 101—105). —The name caseïn is given to the principal proteïd of milk, and caseum to the curd produced by rennet. Caseogen is a term given to the caseïn when that substance is modified by rennet added to decalcified milk. It coagulates on heating, and appears to correspond to the meta-caseïn of Sir W. Roberts (see Edkins, Abstr., 1891, 1272). The lacto-albumin of milk does not belong to this group.

Fibrin and fibrinogen form a group analogous to the caseïns.
     W. D. H.

Nucleoproteïds. By O. HAMMARSTEN (*Zeit. physiol. Chem.*, **19**, 19—37).—In diabetes, there is no longer any doubt that in many cases the sugar originates from proteïds. A knowledge of glucoproteïds (proteïds from which sugar is obtainable by hydrolytic agents) is therefore of practical importance. Such proteïds are obtainable from the mammary gland, the liver, and the pancreas; the present paper relates, however, only to that obtained from the pancreas. The finely divided organ is rapidly boiled in water, and filtered; the filtrate is clear, and yellow in colour. After cooling, if 1—2 per cent. of hydrochloric or 5—10 per cent. of acetic acid, is added, an abundant white flocculent precipitate is formed; this is collected, and purified by re-solution and reprecipitation by dilute alkali and acid respectively. It gives no reduction with Trommer's test; but after boiling for half an hour with 1—2 per cent. hydrochloric, or 2—4 per cent. sulphuric acid, the product gives an abundant reduction. In addition to this reducing substance, there is also a formation of guanine.

The glucoproteïds, like the mucins and the mucoïds, contain less nitrogen (6 to 13 per cent.) than simple proteïds. The present substance, however, has the high percentage of 17·4 of nitrogen. The obtaining of guanine, moreover, suggested the explanation that the substance in question is a nucleïn-like material. The guanine is not simply a mechanical mixture; because no guanine can be obtained from it unless it is previously treated with a mineral acid, and, moreover, elementary analysis of eight preparations gave very concordant results. The mean of the analyses quoted gives C, 43·62; H, 5·45; N, 17·39; S, 0·728; P, 4·48 per cent. There is a very noteworthy percentage of phosphorus. On subjecting it to gastric digestion, the residual nucleïn was found to contain 5·21 per cent. of phosphorus. The amounts of phosphorus in the proteïds and in its nucleïn constituent are thus fairly close, and the solubilities of the substance are like those of the nucleïns. It is termed a nucleo-proteïd. The occurrence of a reducing sugar-like substance from nucleïn is not unique, as Kossel and his pupils have obtained similar results with yeast-nucleïn. This sugar, if such it be, does not ferment with yeast;

like the pentoses, it gives a reaction with phloroglucinol and hydrochloric acid, and by distillation with hydrochloric acid yields furfuraldehyde. It was not, however, obtained in a pure condition. An osazone, partly crystalline, partly amorphous, was obtained ; the latter becoming crystalline after repeated recrystallisations. The crystals were fine needles grouped in rosettes; their melting point was 158—160°. Its properties are not identical with those of any known osazone, and no elementary analysis was made. It appears to be most like the osazones prepared from pentaglucoses by E. Salkowski and M. Jastrowitz (*Cent. med. Wiss.*, 1892, Nos. 19 and 32). The possiblity that it may contain two osazones, one of them being that of glycuronic acid, is also suggested. Glycuronic acid gives the reaction for pentoses.

This nucleo-proteïd, or phospho-glucoproteïd, is the result of the decomposition produced by boiling the proteïd in the pancreatic cells, and resembles those which in the case of other organs have received the names of tissue-fibrinogen (Wooldridge), cytoglobin and präglobulin (Alex. Schmidt), nucleo-albumin (Pekelharing), nucleohiston (Kossel and Lilienfeld) and several other names. This more complicated nucleo-proteïd, the more immediate product of the cells, is split by boiling into coagulated proteïd, and the phospho-glucoproteïd which is the more immediate subject of this paper. It is further suggested that in the case of the pancreas the more complicated nucleo-proteïd is identical with trypsin.

In conclusion, some suggestions regarding nomenclature are made :—

The term *nucleïn* should be restricted to the insoluble residues left after gastric digestion, which consist of compounds of proteïd and nucleïc acid, and which by further decomposition yield xanthine-like substances. The paranucleïns of Kossel which do not yield these so-called nucleïn-bases include a number of very different substances (Liebermann's lecithalbumins, the nucleïn-like substances from ichthulin which also yield a reducing substance, and that from caseïn which does not, Liebermann's artificial nucleïn) and should be called *pseudo-nucleïns.* The term *nucleo-albumin* should be given to substances like caseïn which yield a pseudo-nucleïn, and *nucleo-proteïd* to those which yield true nucleïn. W. D. H.

Constitution of Silk. By H. Silbermann (*Chem. Zeit.*, **17**, 1693—1695).—Crude silk fibre consists of two parts, fibroïn the true thread substance, and a gelatinous body which surrounds it and which is termed sericin. On heating fibroïn with barium hydroxide under pressure, ammonia, acetic acid, carbonic anhydride, oxalic acid, tyrosine (9·5—10 per cent.) alanine, amidobutyric acid, amidoacetic acid, and an amido-acid with the formula $C_4H_7NO_2$, are formed. The following equation represents the hydrolysis of fibroïn,

$$C_{142}H_{214}N_{48}O_{50} + 48H_2O = C_2H_2O_4 + 2H_2CO_3 + C_2H_4O_2 + 6NH_3 +$$
$$2C_9H_{11}NO_3 + 14C_2H_5NO_2 + 14C_3H_7NO_2 + 4C_4H_9NO_2 + 8C_4H_7NO_2.$$
(Tyrosine).   (Amidoacetic   (Alanine).   (Amidobutyric
         acid).   acid).
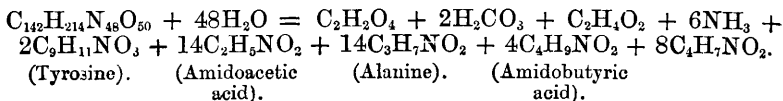
The author gives a constitutional formula for silk, according to which it contains three principal groups, two derived from carbamide and one from tetramide. He does not consider fibroïn a homogeneous substance. In its general reactions, silk behaves like an amido-acid, combining both with basic rosaniline, and with acid azodyes.

J. B. T.

[*Note by Abstractor.*—The molecular weight of fibroïn is given in the original paper as 1970, the above formula corresponds to 3390.]

Hæmatin Hydrochloride and Hydrobromide. By W. Küster (*Ber.*, **27**, 572—578).—Hæmatin hydrochloride was prepared by Nencki and Seiber's method, both from blood and from oxyhæmoglobin, by the action of amylic alcohol and hydrochloric acid ; recrystallized oxyhæmoglobin from horse blood, on treatment with alcohol (93 per cent.) is dehydrated and the product, called parahæmoglobin, on treatment with amylic alcohol and hydrochloric acid also yields hæmatin hydrochloride. The author's analyses of the crystalline compound of hæmatin hydrochloride and amylic alcohol point to the formula $(C_{32}H_{30}N_4FeO_3,HCl)_2,C_5H_{12}O$, instead of $(C_{32}H_{30}N_4FeO_3,HCl)_4,C_5H_{12}O$, as given by Nencki, but only in one experiment was it possible to expel the alcohol completely by heating at 130—135°. By the action of hydrogen bromide on hæmatin in absolute ethylic alcoholic solution the compound

$$C_{32}H_{30}N_4FeO_3,HBr,C_2H_5\!\cdot\!OH$$
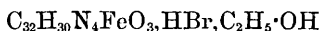
is obtained in small, dark coloured, rhombic crystals. The alcohol is eliminated by treatment with soda.   J. B. T.

Organic Chemistry.

Phenomena of Oxidation and Chemical Properties of Gases.
By F. C. PHILLIPS (*Amer. Chem. J.*, **16**, 163—187; 235—254).—
See this vol., ii, 293, 294.

Calcium Carbide. By H. MOISSAN (*Compt. rend.*, **118**, 50]—
506).—Calcium carbide is obtained by placing an intimate mixture
of 120 grams of calcium oxide from marble and 70 grams of carbon
from sugar in the crucible of the electric furnace, and subjecting it
to the action of a current of 350 ampères and 70 volts for 15 or 20
minutes. The yield is from 120 to 150 grams.

The carbide has the composition C_2Ca, and forms a fused, homo-
geneous, black mass, which cleaves easily, and has a distinctly crys-
talline fracture. The crystals are brilliant and opaque; sp. gr. at $18° =$
2·22. Calcium carbide is insoluble in carbon bisulphide, light petr-
oleum, benzene, and all ordinary reagents. It is not altered when
heated in hydrogen gas, not attacked by nitrogen at 1200°, nor by
silicon or boron at a bright red heat. It is not attacked by sodium or
magnesium at the softening point of glass, nor by tin at a red heat,
nor by iron at a dull red heat, but at a higher temperature it yields
a carburetted alloy of iron and calcium, and with antimony at a red
heat it forms a crystalline alloy containing calcium. Dry chlorine
does not attack the carbide in the cold, but at 245° it becomes incan-
descent, and yields carbon and calcium chloride; bromine behaves
similarly at 350°, and iodine at 305°. At a dull red heat, the
carbide burns in oxygen, with formation of calcium carbonate, and
at 500° it becomes incandescent in sulphur vapour, and yields calcium
sulphide and carbon bisulphide.

Calcium carbide rapidly decomposes water, with evolution of almost
perfectly pure acetylene and development of heat. When the carbide
is heated to dull redness in water vapour, the decomposition is much
less rapid, and the gas evolved consists of hydrogen and acetylene.
Dilute acids behave in the same way as water, but fuming nitric and
sulphuric acid attack it but slightly. Ordinary sulphuric acid, how-
ever, attacks it, and an odour of aldehyde is given off. When heated
in a current of dry hydrogen chloride, the carbide becomes incan-
descent, and the gas evolved contains a large proportion of hydrogen.

When calcium carbide is brought into contact with fused chromic
anhydride, carbonic anhydride is formed, with incandescence. A
solution of chromic acid produces only acetylene. Fused potassium
chlorate or nitrate has little action on the carbide, but at a red heat
oxidation takes place, with incandescence, and calcium carbonate is
formed. Lead peroxide oxidises the carbide, with incandescence,
below a red heat, and the reduced lead contains calcium. When tri-
turated with lead chromate at the ordinary temperature, the carbide
becomes incandescent. If the carbide is heated with absolute alcohol,

in sealed tubes, at 180°, it yields calcium ethoxide and acetylene, $2EtOH + C_2Ca = C_2H_2 + Ca(OEt)_2$. The acetylene is completely absorbed by ammoniacal cuprous chloride, but the acetylide that is formed is black.

If some fragments of calcium carbide are allowed to fall into water saturated with chlorine, bubbles of acetylene are at once evolved, but take fire in contact with the chlorine, and the odour of carbon chlorides is recognisable.   C. H. B.

Barium and Strontium Carbides. By H. Moissan (*Compt. rend.*, **118**, 683—686).—*Barium carbide*, BaC_2, is obtained by heating in a carbon crucible in the electric furnace with a current of 70 vols. and 350 ampères, an intimate mixture of 50 grams of anhydrous barium oxide and 30 grams of carbon from sugar, or a mixture of 150 grams of pure barium carbonate and 25 grams of carbon from sugar. The product is a fused, black, brittle mass, composed of large, lamellar crystals. It is the most fusible of the carbides of the alkali earths; sp. gr. = 3·75.

Strontium carbide, SrC_2, is obtained in a similar manner with 120 grams of strontium oxide and 30 grams of carbon, or 150 grams of strontium carbonate and 50 grams of carbon. The black product has a lustrous, crystalline fracture; sp. gr. = 3·19.

Both carbides are decomposed by water, with formation of the hydroxides and evolution of pure acetylene. The action of concentrated and dilute acids is the same as with calcium carbide (preceding Abstract). With the gaseous hydracids, the carbide becomes incandescent if the temperature is sufficiently high. The following table gives the temperature of incandescence of the three carbides in various other vapours.

	Dry chlorine.	Bromine.	Iodine.
C_2Ca	245°	350°	305°
C_2Sr	197	174	182
C_2Ba	140	130	122

The action of oxygen is also very energetic, but requires a temperature approaching the softening point of glass; under these conditions the barium carbide becomes vividly incandescent. The barium carbide is decomposed, with incandescence, by sulphur at a temperature somewhat above the melting point of the latter, barium and carbon sulphides being formed. At 500°, strontium carbide is decomposed in a similar manner. Selenium decomposes both compounds, with incandescence, producing carbon selenide and a metallic selenide. Silicon and boron have no action at 1000°; nitrogen has no apparent effect, but if the residue is treated with boiling water, after evolution of acetylene, some ammonia is evolved. At a dull red heat, phosphorus produces brilliant incandescence, with formation of a phosphide; arsenic acts with less energy, and requires a higher temperature.   C. H. B.

Hydrophosphocyanic acid. By W. B. Shober and F. W. Spanutius (*Amer. Chem. J.*, **16**, 229—232).—Sodium, free from oxide

and hydroxide, was introduced into a hard, glass tube, and melted in a current of pure, dry hydrogen. When the sodium was fused, the hydrogen current was replaced by a slow current of pure and dry phosphine, the sodium being kept strongly heated. The sodium was gradually converted into a black mass, which was either PH_2Na, $PHNa_2$, or PNa_3, or a mixture of these. Without allowing the apparatus to cool, the phosphine current was then replaced by pure, dry, carbonic oxide, and this passed for an hour. The mass so produced was spontaneously inflammable in air, and was decomposed by water, with evolution of phosphine. Treated with alcohol, a part dissolved, leaving a black residue, but the solution gradually decomposed. It was found impossible to isolate any of the products. When treated with alkalis, the product yields phosphine and formic acid, from which the authors conclude that it contained *hydrophosphocyanic acid*, HCP, the analogue of hydrocyanic acid. The authors hope to investigate this reaction further. L. T. T.

Preparation of Pentadecylic Alcohol from Palmitic acid. By L. PANICS (*Monatsh.*, **15**, 9—16).—The author has prepared pentadecylic alcohol from palmitic acid, by first treating the silver salt with iodine, and then converting the salt, $C_{15}H_{31}\cdot COOC_{15}H_{31}$, thus obtained into the alcohol, $C_{15}H_{31}\cdot OH$ (compare Simonini, Abstr., 1892, 1301; 1893, i, 391). *Pentadecylic bromide*, $C_{15}H_{31}Br$, obtained on heating the alcohol with concentrated hydrobromic acid, at 120°, in sealed tubes, is a brownish oil, which may be solidified by cold, and then melts at 14—15°. On treatment with alcoholic potassium cyanide, and subsequent hydrolysis, it yielded traces of palmitic acid. *Pentadecylic acetate*, $C_{15}H_{31}OAc$, is obtained on heating the alcohol with a large excess of acetic anhydride, in sealed tubes for 20 hours, at 200°. It boils at 230°, under a pressure of 70 mm., has an ethereal odour, and, when strongly cooled, forms a wax-like mass, which melts at 10—11°. On oxidation, the alcohol is converted into pentadecoic acid, $C_{14}H_{29}\cdot COOH$, which is obtained in the form of a white mass, having a mother-of-pearl lustre. This melts at 50°, yields an amorphous, white silver salt, and appears to be identical with the acid (m. p. 51°) obtained from methyl pentadecyl ketone by Krafft (Abstr., 1880, 34). G. T. M.

Compounds of Amidoguanidine and Sugars. By H. WOLFF (*Ber.*, **27**, 971—974).—*Glucosoamidoguanidine hydrochloride*,

$$C_7H_{16}N_4O_5, HCl + H_2O,$$
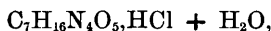
is prepared by the interaction of amidoguanidine hydrochloride and glucose (dextrose) in alcoholic solution; it is deposited in rhombic crystals, and, when dried, melts at 165°. The specific rotatory power $[\alpha]_D = -8\cdot94$. On treatment with dilute hydrochloric acid, the compound is hydrolysed, but the action is incomplete. The *sulphate* crystallises in thin plates, the *acetate* in needles; both are lævogyrate. The *hydrogen sulphate* is liquid; and the *nitrate* crystallises in needles melting at 180°. The *hexacetyl derivative*, $C_9H_{11}N_4O_5Ac_5$

z 2

+ H_2O, is crystalline, and lævogyrate; five acetyl groups are eliminated by the action of acids or alkalis, and the product, $C_9H_{16}N_4O_5 + 2H_2O$, is deposited from water in rhombic crystals; it is dextrogyrate, and has a slightly sweet taste. It is a derivative of dicyanogen, containing the group

$$\begin{array}{c} NH{:}C{\cdot}N{:}N{:}R \\ | \quad | \\ N{:}CMe \end{array}$$

formed from the acetyl compound $NH{:}C(NHAc){\cdot}NH{\cdot}N{:}R$, and is stable towards acids and alkalis. J. B. T.

Yeast-gum. By E. SALKOWSKI (*Ber.*, **27**, 925—926; compare this vol., i, 222).—Since the publication of the paper referred to above, the author has become acquainted with a paper on the same subject published by Hessenland, in the *Zeit. Vereins Rübenzuck-Ind.*, 1892, 671. Hessenland finds that the composition of yeast-gum is expressed by the formula $C_6H_{10}O_5$, whereas according to the author it is $C_{12}H_{22}O_{11}$ (substance dried at 110°). Hessenland finds that on hydrolysis, d-mannose, accompanied by a little dextrose, is formed. The author considers that this seems to show that yeast-gum, at all events, when prepared by the process used by Hessenland, is a mixture of compounds. A. H.

Action of Nitric acid on Aldehydes and Ketones. By H. APETZ and C. HELL (*Ber.*, **27**, 933—948; compare *Ber.*, **14**, 979).— Nitric acid acts on methyl hexyl ketone and on acetophenone with the production of a small amount of a nitrile, whilst no substance of this class is formed when benzaldehyde or furfuraldehyde is thus treated. The action of the acid on acetone is of a complicated character, and has also been investigated by Behrend and Schmidt (Abstr., 1893, i, 303). When acetone is slowly added to cooled fuming nitric acid, a violent action occurs, and an oil is formed, probably a mixture; when this is treated with ammonia, it yields a substance, probably $C_{24}H_{22}N_{18}O_6$, which crystallises in thin scales of a greyish-yellow colour, and characteristic lustre. When treated with acetic chloride, it yields an *acetyl*-derivative of the formula $C_{24}H_{20}N_{18}O_6Ac_2$, which crystallises from alcohol in large, yellowish-white, silky needles melting at 164—165°. It was found impossible to regenerate the original substance by the hydrolysis of this acetyl-derivative. The *benzoyl*-derivative, $C_{24}H_{19}N_{18}O_6Bz_3$, forms small, yellowish-white needles, melting at 193—195°. A *nitro-derivative* can also be obtained, which, like the benzoyl compound, contains three acid groups. It forms long, yellowish-white needles, which decompose with evolution of gas when heated. The compound $C_{24}H_{22}N_{19}O_6$ also yields a bromo-derivative, which forms microscopic, yellow crystals, and appears to have the formula $C_{24}H_{14}N_{18}O_6Br_8$.

When the compound $C_{24}H_{22}N_{19}O_6$ is oxidised with potassium permanganate solution, an acid of the formula $C_3H_3N_3O_3$ is formed, which is being further investigated.

The authors are of opinion that the oil obtained by the action of nitric acid on acetone contains a compound, $COMe{\cdot}C(OH){:}NOH$, from which the crystalline substance of the formula $C_{24}H_{22}N_{18}O_6$ is

obtained by the addition of the elements of ammonia and the elimination of the elements of water. A. H.

Derivatives of Ethereal Salts of Cyanacetic acid. By P. T. MULLER (*Ann. Chim. Phys.*, [7], **1**, 463—547).—By boiling succinic chloride with ethylic sodiocyanacetate in presence of ether, or by mixing the reagents in presence of benzene at the ordinary temperature, there are formed ethylic succinocyanacetate,

$$CH_2 < \begin{matrix} CH_2 \cdot \\ COO \end{matrix} > C{:}C(CN)\cdot COOEt,$$
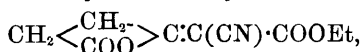
melting at 125—126° (see Abstr., 1891, 1337), and ethylic succinodicyanacetate (Abstr., 1893, i, 143).

If ethylic sodiocyanacetate is boiled with phthalic chloride, two isomeric ethylic phthalocyanacetates are formed (Abstr., 1893, i, 467). When the reaction takes place at the ordinary temperature, a third compound, *ethylic phthalodicyanacetate*, is also formed. It has probably the constitution $CO < \begin{matrix} C_6H_4 \\ O{-} \end{matrix} > C{:}C(CN)\cdot COOEt$, and melts at 158—160°.

Ethylic isonitrosocyanacetate (Abstr., 1891, 1450) melts at 128—129°; two molecular proportions of it combine with one of certain amines, forming compounds which are resolved into the base and isonitrosocyanacetic acid by alkalis. The compounds formed with aniline, orthotoluidine, and paratoluidine, melt at 91—92°, 95°, and 93—94° respectively. When the ethylic salt just described is boiled with ethylic iodide and sodium ethoxide, it is further ethylated, and gives rise to the compound COOEt·C(CN):NOEt, which boils at 125—127° under a pressure of 22—24 mm. Potassium isonitrosomalonate (Baeyer, *Annalen*, **131**, 295) is obtained when ethylic isonitrosocyanacetate is boiled with 33 per cent. potash; whilst isonitrosocyanacetic acid (Wolff and Gans, Abstr., 1891, 897; Söderbaum, *ibid.*, 1184) is formed when the ethylic salt is heated with 7 per cent. soda at 55—60°. When ethylic isonitrosocyanacetate is treated with alcoholic hydrogen chloride, ethylic isonitrosomalonate (Conrad and Bischoff, *Annalen*, **209**, 211) is formed.

Methylic isonitrosocyanacetate (Abstr., 1891, 1450) melts at 119—120°; it crystallises from water with 1H_2O, the hydrated compound melting at 60—65°. When ethylated, it yields the *compound* COOMe·C(CN):NOEt, which boils at 121—124° under a pressure of 23—25 mm. The *benzoyl* derivative, COOMe·C(CN):NOBz, melts at 131—132°. Methylic isonitrosocyanacetate yields methylic isonitrosomalonate when treated with alcoholic hydrogen chloride; this melts at 66—67°.

When ethylic fumarate is heated with ethylic sodiocyanacetate in alcoholic solution, and the product boiled with dilute sulphuric acid, ethylic α-cyanotricarballylate is obtained, which, on hydrolysis with hydrochloric acid, yields the corresponding acid (Simpson, *Annalen*, **128**, 353). Ethylic citraconate reacts in a similar manner with ethylic sodiocyanacetate (see also Abstr., 1892, 1181).

A. R. L.

β-Dibromopropionic acid. By R. Thomas-Mamert (*Compt. rend.*, **118**, 652—653).—*β-Dibromopropionic acid*, $CHBr_2 \cdot CH_2 \cdot COOH$, is obtained by heating β-bromacrylic acid, $CHBr:CH \cdot COOH$, in sealed tubes at 100° with fuming hydrobromic acid. The product is dissolved in benzene, decolorised by means of animal charcoal, and allowed to crystallise. It forms long, rhombic prisms, which melt at 71° (uncorr.). The crystals always show the faces p' and the facettes e', sometimes together with the faces h' or a'. They show the combinations $p\ e'\ h'$, and $p\ e'\ a'$, and the angles observed are aa', 109° 20′; pe', 137° 30′; ee', 85°; pa', 109° 27′. The ratios of the axes $a : b : c = 0.649 : 1 : 0.916$.

When the acid is treated with alcoholic potash, β-bromacrylic acid is obtained, melting at 115°.   C. H. B.

Isocaproic acid and the Solubilities of its Calcium, Barium, and Silver Salts. By J. König (*Monatsh.*, **15**, 17—27).—As contradictory statements have been published regarding the barium and calcium salts of this acid, the author has considered it desirable to synthesise them from pure materials. The method adopted was to prepare ethylic isobutylmalonate, $C_{11}H_{20}O_4$, which boils at 225—226°, by gradually adding sodium ethoxide in alcoholic solution to a mixture of isobutylic iodide and ethylic malonate. From this the free acid $C_7H_{12}O_4$, which forms drusy masses of crystals, and melts at 107°, was obtained; and this, on heating in a reflux apparatus, was resolved into carbonic anhydride and *isobutylacetic acid*. The latter boils at 197—198°, and furnishes the following salts. The *calcium salt*, $Ca(C_6H_{11}O_2)_2 + 5H_2O$, crystallises in slender needles, and has the solubility $s = 7.38 - 0.12402\ (t - 0.8) + 0.00182\ (t - 0.8)^2$. The *barium salt*, $(C_6H_{11}O_2)_2Ba + 4H_2O$, crystallises in needles resembling the calcium salt, and has the solubility $s = 14.28 - 0.11648\ (t - 0.5) + 0.00176\ (t - 0.5)^2$. The *silver salt* forms groups of feathery crystals, and has the solubility $s = 0.1674 - 0.000849\ (t - 1) + 0.0000322\ (t - 1)^2$.   G T. M.

Stereoisomeric α-Methyl-β-chlorocrotonic acids. By R. Otto (*Ber.*, **27**, 948—949; compare Abstr., 1890, 957). When dichlorodimethylsuccinic acid is heated with water at 120—130°, both of the isomeric chlorotiglic acids (melting at 73° and 55°) are formed, and not merely the derivatives of higher melting point, as formerly stated.
A. H.

Derivatives of δ-Hydroxycaproic acid. By J. Zellner (*Monatsh.*, **15**, 29—36).—The starting point of this investigation was Wolff's lactone of normal δ-hydroxycaproic acid,

$$CH_2 < ^{CH_2 \cdot CHMe}_{CH_2 \underline{\quad\quad} CO} > O,$$
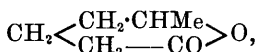
(*Annalen*, **216**, 128), which was dissolved in 10 times its weight of phosphorus oxychloride, and heated in a water bath for two hours with a molecular equivalent of phosphorus pentachloride. On distilling off the phosphorus oxychloride in a vacuum, and boiling the resulting chloride of δ-chlorocaproic acid with alcohol, *ethylic*

δ-*chlorocaproate*, $C_8H_{15}ClO_2$, was obtained. This substance boils, with slight decomposition, at 217—221°, is insoluble in water, dissolves in alcohol and ether, has a peculiar fruity smell, and a sp. gr. 1·04 at 20°. On heating with potassium phthalimide at 180°, it is resolved into a mixture of hydrochloric acid and the ethylic salt of an unsaturated acid, $C_8H_{14}O_2$; and, on heating with alcoholic ammonia at 160—170°, it is converted into a yellow, syrupy compound which is most probably α-methyl-α-piperidone, for, on distillation with zinc dust, it gives rise to α-pipecoline. G. T. M.

Substituted Crotonolactones and Mucobromic acid. By H. B. HILL and R. W. CORNELISON (*Amer. Chem. J.*, **16**, 188—213).—In 1890, Hill and Jackson (Abstr., 1890, 600), by the action of hydrochloric acid on $\beta\delta$-dichloropyromucic acid, obtained a compound $C_4H_3ClO_2$ (melting at 52—53°), and Hill and Sanger (*Proc. Amer. Acad.*, **21**, 158) obtained a similar compound $C_4H_3BrO_2$ (melting at 77°) amongst the products of the action of soda on pyromucic tetrabromide. The authors have studied these and analogous reactions.

β-*Bromocrotonolactone*, $C_4H_3BrO_2$, is formed, with evolution of carbonic anhydride, when $\beta\delta$-dibromopyromucic acid is boiled with concentrated hydrobromic acid, and also by the partial reduction of $\alpha\beta$-dibromocrotonolactone. It melts at 58°, boils under 18 mm. pressure at 140°, and distils with steam. It crystallises in hexagonal plates or truncated prisms, is readily soluble in boiling water, alcohol, and benzene, sparingly in light petroleum. Alkalis cause the separation of alkali bromides, whilst aniline appears to form a substitution derivative which, however, could not be isolated. Bromine, in the cold, forms an additive product, tribromobutyrolactone, $C_4H_3Br_3O_2$, which crystallises in brilliant prisms melting at 63—64°. At 100°, bromine forms mucobromyl bromide; no characteristic oxidation products could be obtained.

$\alpha\beta$-*Dibromocrotonolactone*, $C_4H_2Br_2O_2$, is formed, with evolution of carbonic anhydride, when tribromopyromucic acid is heated at 130° with dilute sulphuric acid (sp. gr. 1·43), or boiled with concentrated hydrobromic acid. It crystallises in six-sided plates or in prisms, is sparingly soluble in cold alcohol, ether, light petroleum, or water, easily so in benzene or chloroform. It melts at 90—91°, boils under 18 mm. pressure at 145°, and distils rapidly with steam. It is very stable towards acids, but unstable towards alkalis, in which it dissolves with formation of alkali bromides, yielding a yellow solution. When dilute potash is employed, 2 mols. of the latter are neutralised, whilst only 1 mol. of potassium bromide is formed, thus leaving but little doubt of its lactonic structure. It is converted into mucobromic acid by boiling with bromine and water. It may be crystallised unchanged from strong nitric acid, but by long boiling with the latter is converted into mucobromic and dibromomaleïc acids. It does not combine with hydrogen sodium sulphite, whilst aniline and phenylhydrazine both remove bromine from it. When treated with zinc and dilute sulphuric acid, a lactone of hydroxycrotonic acid is formed, thus establishing its structure.

When digested with bromine water, the lactone is slowly converted

into mucobromic acid, the oxidation being much hastened by using concentrated hydrobromic acid as the solvent for the bromine. Chromic acid and silver oxide cause more complete oxidation, carbonic anhydride being evolved, and only traces of mucobromic and dibromomaleïc acids formed.

This compound is identical with that erroneously described by Toennies (Abstr., 1879, 918) as dibromofumaric aldehyde. It may also be produced by acting on phosphorus dissolved in carbon bisulphide with an intimate mixture of equivalent weights of iodine and mucobromic acid, or by the reduction of mucobromyl bromide. Bromine does not act on the lactone in the cold, but at 100°, 1 mol. prop. of bromine produces mucobromyl bromide, whilst with excess of bromine, *unsymmetrical dibromomaleïc bromide*, $C_4Br_4O_2$, is formed. The latter crystallises from light petroleum in leaflets which are extremely soluble in alcohol, ether, chloroform, benzene, and carbon bisulphide, more sparingly in light petroleum; it has a strong, suffocating odour like that of the acid dibromanhydrides, and melts at 58—59°. When heated with water, it is slowly converted into dibromomaleïc acid. The authors have as yet been unable to obtain either this compound or an isomeride from dibromomaleïc acid. When the lactone is treated with aniline, aniline bromide is separated and *α-phenylamido-β-bromocrotonolactone* formed. This crystallises in needles or plates; if quickly heated, it melts at 186—187°; if slowly, it decomposes and melts about 165°. It is easily soluble in boiling glacial acetic acid, sparingly in the other organic solvents, and in water.

It dissolves in warm alkalis, and is deposited unchanged if the solution is cooled rapidly; but if the solution is kept warm, decomposition takes place with formation of phenylic isocyanide. *α-Iodo-β-bromocrotonolactone* is formed from the dibromolactone by the action of aqueous hydriodic acid; it forms colourless prisms, colours on exposure to air, and melts at 119—120°; it resembles the dibromoderivative in its properties. Hydriodic acid causes the separation of iodine, and the formation of a viscous, oily substance, but the products could not be isolated. With aniline, it yields α-phenylamido-β-bromocrotonolactone already described, and, on reduction with zinc dust, β-bromocrotonolactone.

The authors consider that the results of their investigations establish for the lactones the respective formulæ

$$\alpha, \ {CX \cdot CO- \atop CH \cdot CH_2} {>} O, \qquad \beta, \ {CH \cdot CO- \atop CX \cdot CH_2} {>}, \ \text{and} \ \alpha\beta, \ {CX \cdot CO- \atop CX \cdot CH_2} {>} O.$$
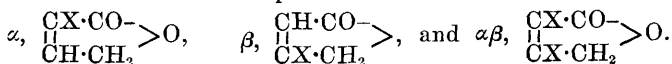
<div align="right">L. T. T.</div>

Substituted Crotonolactones and Mucobromic acid. By H. B. HILL and R. W. CORNELISON (*Amer. Chem. J.*, **16**, 277—307; compare preceding abstract).—*α-Bromocrotonolactone*, $C_4H_3BrO_2$, prepared by the action of zinc dust and acetic acid on bromomaleïc bromide, is also formed by the action of bromine on β-bromopyromucic acid in aqueous solution. It crystallises in long, transparent prisms, melts at 77°, and dissolves freely in boiling water, alcohol, and chloroform, but only sparingly in carbon bisulphide, ether,

benzene, and light petroleum. Bromine converts it into $\alpha\beta$-dibromo-crotonolactone and mucobromic bromide; but when oxidised by bromine water, it yields mucobromic acid and much carbonic anhydride (compare Hill and Sanger, *Proc. Amer. Acad*, **21**, 158; Abstr., 1884, 1305). *α-Phenylamidocrotonolactone* is obtained by the interaction of α-bromocrotonolactone and aniline, also by reducing α-phenylamido-β-bromocrotonolactone with sodium amalgam in alcohol. It crystallises in aggregates of needles, melts at 217—218°, and dissolves readily in boiling alcohol and in hot glacial acetic acid, sparingly in boiling water, hot benzene, or chloroform, and scarcely at all in ether, light petroleum, and carbon bisulphide.

$\alpha\beta$-Dibromocrotonolactone is reduced to crotonolactone by zinc and dilute sulphuric acid at 100°.

Mucochloric bromide, $C_4HCl_2O_2Br$, prepared by the action of phosphorous bromide on mucochloric acid, crystallises in large, transparent plates, melts at 36°, and dissolves readily in alcohol, ether, chloroform, carbon bisulphide, and benzene, but more sparingly in light petroleum. Its alcoholic solution gives a transient, deep purple colour with alkalis.

αβ-Dichlorocrotonolactone, $C_4H_2Cl_2O_2$, is the product obtained by reducing mucochloric bromide by stannous chloride in hydrochloric acid; it crystallises in long, silky needles or in six-sided plates, melts at 50—51°, boils at 114—115° (18 mm.), and dissolves in boiling water, benzene, chloroform, alcohol, ether, and, more sparingly, in carbon bisulphide. It yields mucochloric acid on oxidation. With aniline, it forms *α-phenylamido-β-crotonolactone*, which crystallises in flat prisms, melts at 183°, and dissolves freely in boiling alcohol and boiling chloroform, more sparingly in carbon bisulphide, but not at all in light petroleum. Hydriodic acid converts $\alpha\beta$-dichlorocrotonolactone into *α-iodo-β-chlorocrotonolactone;* this crystallises in long, flat needles, melts at 108—109°, and dissolves in hot alcohol, benzene, or ether, and, more sparingly, in chloroform and carbon bisulphide.

β-Chlorocrotonolactone is prepared by reducing $\alpha\beta$-dichlorocrotonolactone by zinc dust in acetic acid; it crystallises in flat prisms, melts at 25—26°, boils at 124—125° (18 mm.), and dissolves in hot water, alcohol, ether, chloroform, and benzene, but only sparingly in light petroleum. It is also formed when $\beta\delta$-dichloropyromucic acid is heated with acids.

Mucophenoxybromic bromide, $OPh \cdot C_4H_2BrO_2$, produced by the action of phosphorous bromide on mucophenoxybromic acid (*Proc. Amer. Acad.*, **21**, 262; Abstr., 1884, 731), crystallises in needles, melts at 95—96°, and dissolves readily in ether, chloroform, benzene, and hot alcohol, but only sparingly in light petroleum. It is easily reduced to *α-phenoxy-β-bromocrotonolactone*, which is crystalline, and is soluble in ether, chloroform, benzene, glacial acetic acid, and hot alcohol.

When the last-named lactone is dissolved in a hot solution of potassium hydroxide and excess of hydrochloric acid is added, *α-phenoxy-β-bromo-γ-hydroxycrotonic acid* crystallises out; it forms flat, rectangular prisms, with $1H_2O$, melts at about 98°, and dissolves in

alcohol, ether, hot chloroform, and in benzene, but not in light petroleum; the *barium* salt, with $3H_2O$, is soluble in water.

Mucophenoxychloric bromide crystallises in stellate needles, melts at 89—90°, and dissolves freely in hot alcohol. When reduced, it yields *α-phenoxy-β-chlorocrotonolactone*, which crystallises in six-sided plates or flat prisms, melts at 67—68°, and dissolves in ether, chloroform, benzene, carbon bisulphide, hot alcohol, and light petroleum, but not in water. By alkalis it is converted into *α-phenoxy-β-chloro-γ-hydroxycrotonic acid ;* this crystallises in flat, rectangular prisms with $1H_2O$, melts at about 76°, and dissolves readily in alcohol, ether, chloroform, and benzene, less freely in carbon bisulphide and light petroleum, but only sparingly in water, which, when hot, converts it into the lactone; the *barium* salt, with $3H_2O$, is soluble in water.

Mucobromoxime, $C_4H_3Br_2NO_3$, obtained by the interaction of muco-bromic acid and hydroxylamine in alkaline solution, is a granular precipitate without definite melting point; it dissolves in alcohol, ether, and boiling water. When allowed to stand in the liquid from which it is precipitated, it rapidly changes into its *anhydride*, $C_4HBr_2NO_2$, which crystallises in dendritic needles, melts about 117—118°, and dissolves in alcohol, chloroform, and benzene; when heated above its melting point, it changes into its isomeride, dibromo-maleïnimide (Abstr., 1884, 1115); when heated with water, it yields hydrogen ammonium dibromomaleate. The *methyl* derivative of mucobromoxime, $C_4H_2B_2NO_4Me$, is obtained by the reaction between hydroxylamine, mucobromic acid, and boiling methylic alcohol; it crystallises in felted needles, melts at 146—147°, and dissolves in alcohol and hot water, but only sparingly in chloroform, benzene, and cold water.

Mucobromamide, $C_4HBr_2O_2·NH_2$, is produced when ammonia is passed into an ethereal solution of ethylic mucobromate. It crystallises in colourless, dendritic needles, melts, with decomposition, at about 170°, and dissolves readily in hot alcohol.

By reactions analogous to those just described, there were obtained : *Mucochloroxime*, crystallising in felted needles, melting about 90°, and soluble in alcohol and ether ; the *methyl*-derivative of muco-chloroxime crystallising in flat needles, melting, when quickly heated, at 135°, and soluble in alcohol. ether, and chloroform ; *muco-chloramide*, crystallising in oblique prisms, melting at 166°, and soluble in alcohol and hot water ; *mucophenoxybromoxime*, crystallising in long needles, melting at 120—135°, and soluble in alcohol and in ether ; and *mucophenoxychloroxime*, crystallising in aggregates of needles, melting at 112—125°, and soluble in alcohol and in ether.

<div align="right">A. G. B.</div>

cis-**Glutaconic acid.** By E. BUCHNER (*Ber.*, **27**, 881—883).— A comparison of the glutaconic acid prepared from methylic pyrazo-lone-3 : 5-dicarboxylate (*Ber.*, **23**, 703), and that from chloroform and sodium malonate, proves the identity of the two preparations. The pure acid when heated rapidly melts at 138°; under other conditions at 136—137°; and, when slowly heated, at 134°. The acid is *cis*-gluta-conic acid, seeing that when heated with acetic chloride it is converted

into an anhydride which with soda yields the sodium salt of the original acid. When heated at 100°, a cherry-red coloration is produced. A stereoisomeride could not be prepared by heating it with hydrochloric or hydrobromic acid, and the acid remains unchanged. When melted with potassium hydroxide, it is decomposed, with the production of malonic acid, a part of the latter being also decomposed into acetic acid. The *anhydride* crystallises in flat, pale yellow needles, and melts at 87°. E. C. R.

Elimination of Carbonic Oxide from Ethylic Oxalacetate and its Derivatives. By W. WISLICENUS (*Ber.*, **27**, 792—798).— When ethylic oxalacetate, or a derivative of it, is heated at 150—190°, or distilled under ordinary pressure, it loses carbonic oxide and yields ethylic malonate, or a derivative, $COOEt \cdot CO \cdot CH_2 \cdot COOEt = CO + CH_2(COOEt)_2$. This reaction, which it is proposed to term "carbon monoxide elimination" ("Kohlenoxydspaltung"), is the main one in the case of the derivatives, but with ethylic oxalacetate itself other reactions take place in addition. Some condenses forming products of higher boiling point, and some reacts with the water thus formed, yielding carbonic anhydride and ethylic pyruvate, $COOEt \cdot CH_2 \cdot CO \cdot COOEt + H_2O = CO_2 + EtOH + CH_3 \cdot CO \cdot COOEt$.

Ethylic oxalacetate, methyloxalacetate, and oxalosuccinate have been found to undergo the above-mentioned change, yielding respectively ethylic malonate, ethylic methylmalonate (isosuccinate), and *ethylic ethenyltricarboxylate*, $COOEt \cdot CH_2 \cdot CH(COOEt)_2$. The last substance boils at 276° (uncorr.; at 152—153° under 14 mm. pressure). The *acid* itself melts at 159°. Its *sodium salt* and *barium salt*, with $1H_2O$, were prepared. When heated, it decomposes into carbonic anhydride and succinic acid. C. F. B.

Decomposition of Tartaric and Citric acids by Sunlight. By W. SEEKAMP (*Annalen*, **278**, 373—374).—A 5 per cent. solution of tartaric acid, in which 1 per cent. of uranic oxide was dissolved, was exposed to sunlight. Gas was soon evolved, and the liquid became green, due to the reduction of the uranic oxide. After a month, the liquid was examined, and found to contain aldehyde, which was removed by distillation. The residual liquid, which had an acid reaction, was neutralised with lead hydroxide, and from the resulting precipitate, on decomposition with hydrogen sulphide, tartaric, malic, and succinic acids were obtained, whilst the filtrate contained a cupric reducing substance, together with, perhaps, propionic acid. Citric acid behaved in a similar manner. A. R. L.

Dissociation of Potassium Hydrogen Tartrate. By A. A. NOYES (*Zeit. physikal. Chem.*, **13**, 417—418).—The dissociation was determined by the inversion of sugar, according to Trevor's method (*ibid.*, **10**, 321), a platinum tube being employed, and the rate of inversion compared with that induced by acetic acid. The reaction constant of a 0·0351 solution of potassium hydrogen tartrate was 0·00422; that of a 0·00785 solution of acetic acid was 0·00463; whence if x is the degree of dissociation of the hydrogen atom of the salt, and α that of the acid, $0.00785 \ x : 0.0351 \ x =$

0·00467 : 0·00422. For the dilution employed, $\alpha = 4·67$ per cent., whence $x = 0·944$ per cent., and the value for the dissociation constant of the acid ions $H·C_4H_4O_6$ is 0·00012. From these numbers, the author deduces the composition of the solution of the salt, which he calculates to contain about 8 per cent. of free undissociated acid.

<div align="right">L. M. J.</div>

Solubility of Potassium Hydrogen Tartrate. By A. A. NOYES and A. A. CLEMENT (*Zeit. physikal. Chem.*, **13**, 412—416).—The influence of several salts on the solubility of potassium hydrogen tartrate was investigated. The salts used were the chloride, chlorate, bromide, iodide, nitrate, acetate, and sulphate of potassium. Blarez's conclusion that potassium salts in equivalent amounts have equal effects in lowering the solubility appears to be only a first approximation. The authors' experiments show that the three haloïds have equal effect; the nitrate has a somewhat smaller effect, the chlorate smaller still, and the sulphate the least of all the salts examined. Acetic acid causes an increase in the solubility. This is explained by the fact that the acetic acid is only slightly dissociated, so that the hydrogen ions from the acid tartrate unite with the acetic acid ions to form undissociated acetic acid. The small effect of potassium sulphate is similarly explained, sulphuric acid being only moderately dissociated. The solubility of the salt is also increased by hydrogen chloride or salts of sodium, owing, in the latter case, to the formation of undissociated sodium salts.

<div align="right">L. M. J.</div>

A Cyclic Analogue of Ethylic Ketipate. By W. DIECKMANN (*Ber.*, **27**, 965—966).—Ethylic suberate, like ethylic pimelate, is converted into a β-ketonic acid by the action of sodium (this vol., i, 173), but ethylic glutarate and ethylic sebate do not react. That this is due to the arrangement of the atoms in space is shown by the production of *ethylic* 1 : 2-*diketopentamethylene*-3 : 5-*dicarboxylate*,

$$CH_2 \diagdown \genfrac{}{}{0pt}{}{CH(COOEt)·CO}{CH(COOEt)·CO},$$

by the interaction of sodium, ethylic glutarate, and ethylic oxalate, at 120°. It crystallises from alcohol in pale yellow, lustrous needles, from ether in broad, highly refractive prisms, melts at 118°, gives a red coloration with ferric chloride in alcoholic solution, and is completely analogous to ethylic ketipate from ethylic oxalate and ethylic acetate. The *sodium salt* is yellow and crystalline.

<div align="right">J. B. T.</div>

Reduction of Ethylic Diazoacetate. By R. JAY and T. CURTIUS (*Ber.*, **27**, 775—778).—Precise practical details are given for the preparation of hydrazine hydrate from chloracetic acid; for these the paper must be consulted. When ethylic diazoacetate, $N_2:CH·COOEt$, is reduced with ferrous hydroxide in feebly alkaline solution, *hydraziacetic acid*, $N_2H_2:CH·COOH$, is formed, and not hydrazineacetic acid, $NH_2·NH·CH_2·COOH$, which has not yet been obtained. When the solution is acidified, hydrazine and glyoxylic acid are formed. Silver hydraziacetate was prepared.

<div align="right">C. F. B.</div>

Ethylic Hydrazicarboxylates and Azocarboxylates. By T. CURTIUS and K. HEIDENREICH (*Ber.*, **27**, 773—774).—*Ethylic hydrazicarboxylate*, $N_2H_2(COOEt)_2$, is obtained by the action of hydrazine hydrate on ethylic chloroformate in alcoholic solution; it crystallises in colourless prisms, melts at 130°, and decomposes and boils at 250°; it is very stable to acids and alkalis, being only hydrolysed by them on boiling, when it yields hydrazine, carbonic anhydride, and alcohol. When it is dissolved in strong nitric acid, and a little fuming nitric acid added, it is slowly oxidised to *ethylic azocarboxylate* $N_2(COOEt)_2$. This is an orange-yellow oil, which boils at 106° under 13 mm. pressure; it is very easily hydrolysed; cold aqueous ammonia converts it into Thiele's azodicarboxamide (Abstr., 1892, 1430); boiling with dilute acid always results in the regeneration of some hydrazicarboxylate. C. F. B.

Affinity Constants of some Sulphur Compounds. By J. M. LOVÉN (*Zeit. Physikal Chem.*, **13**, 550—560).—The author has determined the affinity constants of a number of sulphur-derivatives of acetic and propionic acids, employing Kohlrausch's method. The results for 25° are given in the accompanying table.

Acid.	$k.$
$S(CH_2 \cdot COOH)_2$	0·049
$S(CHMe \cdot COOH)_2$ (m. p. 125°)	0·049
„ (m. p. 109°)	0·044
$S(CH_2 \cdot CH_2 \cdot COOH)_2$	0·0078
$COOH \cdot CH_2 \cdot S \cdot CHMe \cdot COOH$	0·048
$COOH \cdot CH_2 \cdot S \cdot CH_2 \cdot CH_2 \cdot COOH$	0·025
$COOH \cdot CH_2 \cdot CH_2 \cdot S \cdot CHMe \cdot COOH$	0·021
$S_2(CHMe \cdot COOH)_2$	0·090
$S_2(CH_2 \cdot CH_2 \cdot COOH)_2$	0·0090
$S_3(CHMe \cdot COOH)_2$	0·080
$SO_2(CH_2 \cdot COOH)_2$	1·30
$SO_2(CHMe \cdot COOH)_2$	1·03
$SO_2(CH_2 \cdot CH_2 \cdot COOH)_2$	0·024
$COOH \cdot CH_2 \cdot SO_2 \cdot CHMe \cdot COOH$	1·24
$COOH \cdot CH_2 \cdot SO_2 \cdot CH_2 \cdot CH_2 \cdot COOH$	0·51

The increase in strength for the oxidation of S to SO_2 is in all cases very marked. From the value of k for the trithio-compound, the author concludes that its constitution is as given, and not of the form $S[CMe(SH) \cdot COOH]_2$, for which he estimates the value of k should be about 0·30. L. M. J.

The Benzene Nucleus. By W. VAUBEL (*J. pr. Chem.*, [2], **49**, 308—316; compare Abstr., 1891, 1343).—It is evident from the work of Crum Brown and Gibson (Trans., 1892, 367), of Schöpff (Abstr., 1892, 335), of P. Fischer (Abstr., 1892, 331), and of the author (Abstr., 1892, 1187), that the carbon atoms in the benzene nucleus which are in the meta-position with regard to each other are more closely related than are those in the ortho- or para-position. No con-

figuration of the benzene molecule which does not take cognisance of the difference between the behaviour towards reagents of ortho- and para-derivatives on the one hand, and of meta-derivatives on the other hand, and of the proximity, as it were, of the meta-positions, can correctly represent the constitution of benzene. The author's formula has been already described (Abstr., 1891, 1343), and is expressed by the accompanying figure, in which the continuous and broken lines represent tetrahedra on opposite sides of the plane of the paper.
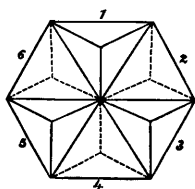
It is shown that this formula is in accord with Baeyer's investigations on the reduction products of benzene derivatives, and with the fact that meta-derivatives do not tend to form anhydrides.

<div style="text-align:right">A. G. B.</div>

Action of Bromine on Paraxylene. By J. ALLAIN LE-CANU (*Compt. rend.*, **118**, 534—535).—Tribromo-paraxylene, $C_8H_7Br_3$, is obtained, together with the dibromo-derivative, by the action of bromine on paraxylene in presence of sunlight. It crystallises from ether in rhombic lamellæ, flattened along the base p, and limited by the faces m, h', the angle of the faces m being very nearly 120°. The crystals are almost always macled along m, and tend towards hexagonal symmetry; they melt at 116°, with some decomposition. When hydrolysed, the tribromo-derivative yields the aldehyde-alcohol, $CHO \cdot C_6H_4 \cdot CH_2 \cdot OH$, a colourless, oily liquid, which is very soluble in ether, and does not boil below 200°. The latter yields a hydrazone, $OH \cdot CH_2 \cdot C_6H_4 \cdot CH{:}N \cdot NHPh$, a pale yellow powder, which alters rapidly even when not exposed to light, and is only slightly soluble in boiling water.

<div style="text-align:right">C. H. B.</div>

Cholesterol. By J. MAUTHNER and W. SUIDA (*Monatsh.*, **15**, 85—115).—*Cholestene (Hydrocholesterylene)*, $C_{27}H_{46}$, may be obtained by reducing cholesterylic chloride, in amylic alcoholic solution, with sodium (compare Walitzky, this Journ., 1877, i, 58). It forms colourless needles, melts at 89—90°, and has a rotatory power in chloroform solution of $[\alpha]_D = -56\cdot29°$. When a solution in chloroform is heated with bromine, *α- and β-cholestene dibromides*, $C_{27}H_{46}Br_2$, are formed. The α-compound crystallises in rhombic prisms, $a : b : c = 0\cdot5456 : 1 : 0\cdot5343$; it melts at 141—142°, and rapidly decomposes at a higher temperature. The β-compound crystallises in colourless scales, melts at 106°, and when dissolved in alcohol is slowly converted at ordinary temperatures, or more rapidly, but with partial decomposition, on boiling, into the α-compound. *Cholestene dichloride*, $C_{27}H_{46}Cl_2$, is obtained in a similar manner to the dibromides, and crystallises in scales, which melt at 119—120°, an oily substance,

probably an isomeride, being simultaneously formed. All the above-mentioned additive products, on reduction with sodium in amylic alcoholic solution, give cholestene, and not cholestane, $C_{27}H_{48}$, as was expected. *Chlorocholestene dichloride*, $C_{27}H_{45}Cl_3$, is obtained on passing dry chlorine into a solution of cholesterylic chloride in chloroform. It crystallises from a mixture of alcohol and acetone in scales, and melts at $\overline{1}06°$. *Cholesterol dichloride*, $C_{27}H_{46}OCl_2 + H_2O$, is formed on passing chlorine into a solution of cholesterol in chloroform. It is anhydrous at $100°$, and in that state softens at $125°$ and melts at $136°$. If iodine is present during the absorption, a resinous substance *dichlorocholesterene dichloride*, $C_{27}H_{44}Cl_4O$, is formed in addition to the dichloride described. *Cholesterylic acetate dichloride*, $C_{27}H_{45}Cl_2 \cdot OAc$, may be obtained either by the action of chlorine on cholesterylic acetate, or by warming cholesterol dichloride with acetic anhydride.

On treatment with nitrous acid, cholesterylic chloride is converted into *nitrocholesterylic chloride*, $C_{27}H_{44}Cl \cdot NO_2$, which melts at $149°$, and has not the power of directly uniting with bromine. When the nitrous gas was previously passed over calcium chloride, it was found to contain a considerable quantity of chlorine, probably in the form of nitrosyl chloride, and to give rise to the compound $C_{54}H_{89}Cl_4N_3O_3$. This crystallises from its hot solution in glacial acetic acid, in beautiful, long, colourless, needles, melts at $110°$, and when heated with an alcoholic solution of potassium acetate is converted into a compound $C_{54}H_{89}Cl_2N_3O_4$, which melts at $147°$. By the interaction of cholestene and nitrous acid, a compound was obtained in pale yellow crystals, melting at $105°$; it probably has the composition $C_{27}H_{45}NO_2$ or $C_{27}H_{43}NO_2$, and, like the product from cholesterylic chloride mentioned above, is a fully saturated compound. Endeavours to prepare Preis and Raymann's crystalline dinitrocholesterol, which melts at $120—121°$ (compare Abstr., 1879, 634), were without success, the amorphous product obtained, having the composition $C_{18}H_{27}NO_4$, as shown by the analyses of its dull yellow *silver salt*, $C_{18}H_{26}NO_4Ag$, and bright green *copper salt*, $(C_{18}H_{26}NO_4)_2Cu$.

From their investigations of the cholestene group, the authors conclude, (i) that those compounds, to which cholesterol itself belongs, take up only one molecule of a halogen, and that the saturated hydrocarbon from which they are derived is represented by the formula $C_{27}H_{48}$, and must therefore contain closed chains; (ii) that there exists in the nuclear portions of the compounds at least one asymmetric carbon atom; (iii) that since no halogen acid is eliminated when the compounds are treated with alcoholic potash, the group $\cdot CH\colon CH\cdot$ is absent, the remarkable stability of the compounds being probably explained by the presence of two directly linked carbon atoms, to each of which two other carbon atoms are immediately attached; (iv) the unknown position taken up by the halogen makes it uncertain whether all the closed chains in the compounds are fully saturated; (v) that the two dibromides described above are probably stereo-isomerides, since one of them is readily converted into the other. G. T. M.

Constitution of Polythymoquinone. By K. LAGODZINSKI and M. MATEESCU (*Ber.*, **27**, 958—961). The formula

$$C_6H_2MePr\begin{matrix}O\cdot O\\O\cdot O\end{matrix}C_6H_2MePr,$$
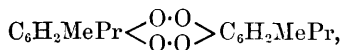
given by Liebermann and Ilinski in 1885 to polythymoquinone, is confirmed by the authors' cryoscopic molecular weight determinations, and they suggest that it should be termed dithymoquinone.

In addition to the phenylhydrazone, benzeneazothymol,
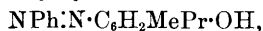
$$NPh\dot{:}N\cdot C_6H_2MePr\cdot OH,$$

is formed by the interaction of phenylhydrazine and dithymoquinone, being probably produced from the hypothetical thymoquinonephenylhydrazone $NHPh\cdot N\dot{:}C_6H_2MePr\dot{:}O$, since thymoquinone and phenylhydrazine hydrochloride yield hydroxythymoquinone and nitrogen. *Benzeneazothymol hydrochloride* is reddish-violet, and undergoes dissociation by prolonged treatment with water. Azophenol and its ethyl ether also form hydrochlorides.   J. B. T.

Orthanisidine. By R. DIEFENBACH (*Ber.*, **27**, 928—933).—This investigation was undertaken with the object of preparing ethylene-phenylenediamine, $C_6H_4\begin{matrix}NH\\NH\end{matrix}C_2H_4$, and phenomorpholine,

$$C_6H_4\begin{matrix}O—\\NH\end{matrix}C_2H_4,$$
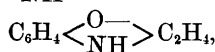
(Knorr, Abstr., 1889, 1218) from amidoethylorthanisidine and amidoethylorthamidophenol.

Orthanisidoethylphthalimide, $C_8H_4O_2\dot{:}N\cdot CH_2\cdot CH_2\cdot NH\cdot C_6H_4\cdot OMe$, is obtained by the action of orthanisidine on bromethylphthalimide, and forms yellow crystals melting at 118—119°. When it is treated with hydrochloric acid, *amidoethylorthanisidine hydrochloride*,

$$OMe\cdot C_6H_4\cdot NH\cdot CH_2\cdot CH_2\cdot NH_2,2HCl,$$

is obtained in greenish-white crystals, melting at 156°. The *free base* is a colourless oil, which boils at 277—280°. The *picrate*, $C_9H_{14}N_2O,2C_6H_3N_3O_7$, separates from alcohol in pale yellow crystals. The base combines with carbon bisulphide to form the corresponding *dithiocarbamate*, $(C_9H_{14}N_2O)_2CS_2$, which crystallises in colourless needles, melting at 123°. *Anisidoethylphenylthiocarbamide*,

$$NHPh\cdot CS\cdot NH\cdot C_2H_4\cdot NH\cdot C_6H_4\cdot OMe,$$
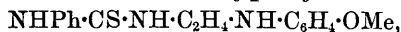
obtained by the combination of the base with phenylic thiocarbimide, melts at 117—118°. *Dibenzoylamidoethylorthanisidine* forms colourless crystals melting at 134—135°. The free base is not converted by simple heating into ethylenephenylenediamine. *Amidoethylorthamidophenol*, $NH_2\cdot C_2H_4\cdot NH\cdot C_6H_4\cdot OH$, cannot be obtained from amidoethylorthanisidine by treatment with nitrous acid or by heating it with hydrochloric acid, but is formed when it is heated with hydriodic acid, and can be more readily prepared in the same way from orthanisidoethylphthalimide. The *hydriodide*, $C_9H_{12}N_2O,2HI + H_2O$, forms colourless crystals, which cannot be recrystallised, and melt at 106—107°. The *sulphate* is almost insoluble in cold water and can

be recrystallised from hot water. The *hydrochloride* separates from amylic alcohol in pale-lilac coloured crystals, which do not melt below 300°. The *picrate* melts at 158—160°. *Tetrabenzoylamidoethylorthamidophenol*, $C_8H_8N_2OBz_4$, forms colourless crystals, melting at 63—65°. The free *amidoethylorthamidophenol* boils at 280—285°, melts at 154—155° and forms colourless crystals. It is not converted by simple heating into phenomorpholine. A. H.

Action of the Salts of Diazobenzene on Methylic and Ethylic Alcohols. By J. L. BEESON (*Amer. Chem. J.*, **16**, 235—254).—The decomposition of diazobenzene nitrate with methylic alcohol produces the alkoxy-benzene, whether the change occurs at the ordinary temperature or at the boiling point of the alcohol. Orthonitrophenol, attributed to a molecular rearrangement of the diazobenzene nitrate, is also formed, and is partially converted into 2:4-dinitrophenol by the action of liberated nitric acid. When paranitrophenol is produced it may be traced to the nitration of phenol formed by the action of water, present in the alcohol, on the diazobenzene nitrate.

In the case of the action of diazobenzene nitrate on ethylic alcohol, a high temperature increases the alkoxy-reaction, whilst a low temperature increases the hydrogen reaction (formation of benzene). The presence of a small amount of water increases the alkoxy-reaction.

Excess of alkali or of zinc dust, respectively, brings about the hydrogen reaction (formation of benzene and diphenyl) in the decomposition of diazobenzene nitrate by either alcohol. The same change is produced by the interaction of diazobenzene nitrate with sodium methoxide and ethoxide in solution in their respective alcohols, and in all these three cases there appears to be two reactions, one between the diazo-salt and the neutralising agent, giving the diphenyl reaction, and the other between the diazo-salt and the alcohol giving the hydrogen reaction.

The decomposition of diazobenzene sulphate by methylic alcohol gave nothing but the alkoxy-derivative. A. G. B.

Action of Ammonia on Diazobenzene. By H. v. PECHMANN and L. FROBENIUS (*Ber.*, **27**, 898—900).—The authors conclude that the unstable compound obtained by Griess, by acting on diazobenzene with ammonia, is bisdiazobenzeneamide, since they have obtained bisparadiazotolueneamide from paradiazotoluene in the same way.

Bisparadiazotolueneamide, $NH(N:NC_7H_7)_2$, is obtained by gradually adding a concentrated solution of paradiazotoluene chloride to an excess of ammonia at 0°. It crystallises in lustrous, yellow needles, explodes at 82—83°, or on concussion or by rubbing, and has feebly acid and basic properties. When boiled with acids, it decomposes into nitrogen, cresol, and toluidine. E. C. R.

Diazo- and Isodiazo-compounds. By E. BAMBERGER (*Ber.*, **27**, 914—917; see also Schraube and Schmidt; this vol., i, 237, and Bamberger, this vol., i, 295).—Benzenediazoic acid is most easily prepared by adding potassium isodiazobenzene to an alkaline solution

of potassium ferricyanide, and allowing the mixture to remain about 24 hours.

The author has been unable to obtain isodiazo-compounds from acetylated nitrosamines. When nitrosoacetanilide is treated with potassium hydroxide, diazobenzene is obtained. This behaviour of acetylated nitrosamines and the fact that they give the colour reactions of diazo-compounds when treated with α-naphthylamine is evidence for the existence of the two forms $R \cdot NAc \cdot NO$ and $R \cdot N_2 \cdot OAc$.

E. C. R.

Action of Nitrous Acid on Amidoparadichlorobenzene. By P. HERSCHMANN (*Ber.*, **27**, 767—768).—The compounds supposed by Zettel (this vol., i, 22) to be tetrachlorodiazoamidobenzene and paradichlorophenylhydrazine have in reality this constitution, for it is possible to convert the latter, by treating it with iodine solution, into dichloriodobenzene; this boils at 250—251°, and yields a mononitroderivative which crystallises in almost colourless needles, and melts at 82°. C. F. B.

Velocity of Transformation of Aldoximes into Acid Nitriles. By A. HANTZSCH (*Zeit. physikal. Chem.*, **13**, 509—530).—The paper contains the results of researches undertaken with the object of determining the effect of various radicles on the rate of decomposition of the acetates of synaldoximes into acid nitriles,

$$CH_3 \cdot COO \cdot N\ddot{:}CHR \rightarrow N\ddot{:}CR + CH_3 \cdot COOH.$$
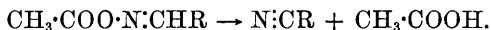
The greatest possible care had to be taken in the preparation of the aldoximes, and especially during the formation of the acetate, a matter frequently of very great difficulty, owing to the extraordinary ease with which many of the compounds were converted into the nitrile during the reaction. The decomposition may be induced by an alkali carbonate, the reaction in this case taking place in two stages, and being therefore of the second order; constant values, however, were not obtainable by the use of sodium carbonate, as it was found that water itself acted as a catalytic agent and effected the decomposition. Water was, therefore, used for the purpose, the compound being dissolved to about N/100 solution in a mixture of 3 vols. alcohol to 2 vols. water, with the addition of a little sodium acetate to prevent etherification of the acetic acid produced. Meta-derivatives as a rule could not be converted into acetate, owing to their ready decomposition. The reaction being of the first order, the velocity constant is given by the equation $C = \dfrac{1}{t} \log \dfrac{A}{A-x}$, where $\dfrac{x}{A}$ is the fraction of the original substance remaining after t minutes. The results are given in the following table (p. 331).

The cyano-derivative gave a decreasing instead of a constant value for C, possibly due to the hydrolysis of the cyanogen group by the acetic acid formed, whilst constant values could not be obtained in the para-nitro-compound, in cinnamic aldoxime, or in para-tolylform-oxime. The data are insufficient for a complete elucidation, but variation of the velocity with the chemical nature is plainly indicated, and especially is this so in the case of the halogen compounds.

c.

Metanitrosynbenzaldoxime acetate. $C_9H_8N_2O_4$ ..	0·000128
Parachlorobenzaldoxime acetate, $C_9H_8(Cl)NO_2$..	0·000371
Thiophensynaldoxime acetate, $C_7H_7SNO_2$	0·000408
Paramethoxybenzaldoxime acetate, $C_{10}H_{11}NO_3$ ..	0·000410
Piperonalsynaldoxime acetate, $C_{10}H_9NO_4$	0·000474
Paratolylsynaldoxime acetate, $C_{10}H_{11}NO_2$	0·000475
Benzaldoxime acetate, $C_9H_9NO_2$	0·000552
Paraethoxybenzaldoxime acetate, $C_{11}H_{13}NO_2$	0·000564
Parabromobenzsynaldoxime acetate, $C_9H_8BrNO_2$	0·000619
Paraiodobenzaldoxime acetate, $C_9H_8INO_2$	0·000696
Paracyanobenzaldoxime acetate, $C_9H_8(CN)NO_2$..	0·0008 (?)
Paranitrobenzaldoxime acetate, $C_9H_8N_2O_4$ (at least)	0·0008

Pariodobenzaldehyde melts at 77° (not at 73° as stated by Jackson and White); the *antioxime* melts at 122°; the *synoxime* at 160°, and its acetate at 127°.

Paracyanobenzaldehyde melts at 92°; the *antioxime* at 180°, the *synoxime* at 143—145°, and its *acetate* at 122—124°.   L. M. J.

Transformation of Acid-azides into Derivatives of Alkylamines (Substitution of NH_2 for COOH). By T. Curtius (*Ber.*, **27**, 778—781).—Acid-azides when warmed gently in alcoholic solution lose nitrogen and form carbamates (urethanes). For example, benzoylazide, $CPhO·N_3$ yields the phenylcarbamate $NHPh·COOEt$; nitrobenzoylazine, hippurazide, and fumurazide behave in a similar manner. When boiled with water, benzoylazide yields diphenylcarbamide, $CO(NHPh)_2$, but probably ethylic phenylcarbamate is formed as an unstable intermediate product. With bromine, benzoylazide yields dibromocarbanil, $NPhBr_2CO$, which loses bromine when heated, forming carbanil, $NPh:CO$, and this is converted into diphenylcarbamide by water.

To convert an acid, $R·COOH$, into an amine, it is thus necessary to make the ethereal salt, $R·COOEt$, to get the hydrazide, $R·CO·NH·NH$, from this by the action of hydrazine hydrate, to treat it with nitrous acid to form the azide, $R·CO·N_3$, to boil this with alcohol to get the carbamate, $R·NH·COOEt$, or with water to get the carbamide, $(R·NH)_2CO$, and to convert either of these, by heating with strong hydrochloric acid at 120°, into the amine, $R·NH_2$.   C. F. B.

Dibromogallanilide and its Triacetyl-derivative. By P. Cazeneuve (*Compt. rend.*, **118**, 540—541).—When finely powdered gallanilide is added to chloroform containing the requisite quantity of bromine, dibromogallanilide is formed with development of heat. It crystallises from dilute methylic alcohol in small, white needles; it is only slightly soluble in boiling water, but crystallises from it with $5H_2O$, which it loses at 100°. Dibromogallanilide does not melt without decomposition; it dissolves in alcohol and in ether. With ferric chloride, its solutions give a blue coloration. When heated with concentrated hydrochloric acid in sealed tubes at 150°, it yields aniline, and a blackish product which probably results from the alteration of

2 *a* 2

the dibromogallic acid. Bromination, therefore, takes place in the benzene nucleus.

Boiling acetic chloride has no action on dibromogallanilide, but acetic anhydride attacks it somewhat rapidly, yielding a triacetyl-derivative, which crystallises from strong alcohol acidified with acetic acid in small, white crystals, insoluble in benzene or light petroleum, but soluble in chloroform. It does not melt without decomposition, and gives no coloration with ferric chloride. When boiled with alcohol, it yields a di- or monacetyl-derivative, which gives a coloration with ferric chloride.

Attempts to remove the bromine atoms from the nucleus by hydrolysis were unsuccessful. C. H. B.

Benzoic Halogen Amides. By C. E. LINEBARGER (*Amer. Chem. J.*, **16**, 216—218).—*Benzoic bromamide*, $COPh \cdot NHBr$, was obtained by acting on benzamide with bromine. It crystallises in small plates, melts at 171°, and is soluble in alcohol, alcohol and ether, and benzene. Attempts to substitute the bromine radicle were unsuccessful. Benzoic chloramide was obtained by Bender (Abstr., 1887, 44) by the action of bleaching powder on benzamide. It may also be readily obtained by acting on benzoic bromamide with hydrochloric acid. No corresponding iodo-compound could be obtained. L. T. T.

Action of Phenylic Isocyanate on Amido-acids. By C. PAAL (*Ber.*, **27**, 974—979).—Phenylic isocyanate readily combines with the sodium or potassium salts of amido-acids to form phenylureïdo-derivatives, but with the free acids the reaction is more complex (compare Kühn, Abstr., 1885, 260).

Phenylureïdacetic acid, $NHPh \cdot CO \cdot NH \cdot CH_2 \cdot COOH$, crystallises from water in long, concentric needles, melts at 195°, and is readily soluble in alkalis and alkali carbonates. The *sodium, barium, zinc*, and *copper* salts are crystalline, the last being bluish-green. The *ammonium salt* readily undergoes dissociation; the *aluminium salt* is amorphous; the *silver salt* is stable, and crystallises in colourless, stellate needles; the *ethylic salt* crystallises in long, thin prisms melting and decomposing at 114°.

α-Phenylureïdopropionic acid, $NHPh \cdot CO \cdot NH \cdot CHMe \cdot COOH$, prepared in a similar manner to the preceding acid, has already been obtained by Kühn.

Orthophenylureïdobenzoic acid, $NHPh \cdot CO \cdot NH \cdot C_6H_4 \cdot COOH$, prepared from sodium orthamidobenzoate and phenylic isocyanate, crystallises from dilute alcohol in colourless, needle-like aggregates melting at 181°. The *silver salt* is stable; the *zinc, lead*, and *copper* salts are amorphous. By the action of hydrogen chloride on the acid in alcoholic solution, or by heating the ammonium salt in aqueous solution, 3′-phenyl-2′ : 4′-diketotetrahydroquinazoline, $C_6H_4 \begin{array}{l} NH \cdot CO \\ CO \cdot NPh \end{array}$ (m. p. 272°), is formed. The yield by the former method is 70 per cent. of the theoretical. *Ethylic orthophenylureïdobenzoate* is obtained in small quantity along with the quinazoline; it is readily soluble, and

crystallises in needles melting at 144°. Metaphenylureïdobenzoic acid melts at 264°, not 270° as stated by Kühn. J. B. T.

Ureïdes of Phenyloxamethane. By H. SCHIFF and A. OSTRO-GOVICH (*Ber.*, **27**, 961—963).—Urethanophenyloxamethane,

$$COOEt \cdot NH \cdot C_6H_4 \cdot NH \cdot CO \cdot COOEt,$$
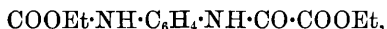
is prepared by the action of ethylic oxalate on paramidophenyl-urethane, $NH_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot COOEt$ (this vol., i, 236), and crystal-lises in acicular plates melting at 131—132°. On treatment with alcoholic ammonia, *urethanophenyloxamide*,

$$COOEt \cdot NH \cdot C_6H_4 \cdot NH \cdot CO \cdot CO \cdot NH_2,$$

is formed, crystallising in colourless needles, and melting and decom-posing at 301—302°. The *anilide*, $COOEt \cdot NH \cdot C_6H_4 \cdot CO \cdot CO \cdot NHPh$, forms colourless, flocculent crystals, consisting of microscopic needles, is sparingly soluble, and melts at 351° (corr.). Paramido-phenylcarbamide, $NH_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, and ethylic oxalate yield *uramidophenyloxamethane*, $NH_2 \cdot CO \cdot NH \cdot C_6H_4 \cdot NH \cdot CO \cdot COOEt$, crystal-lising in colourless, slender needles, and melting at 210—211°. The *amide*, $NH_2 \cdot CO \cdot NH \cdot C_6H_4 \cdot NH \cdot CO \cdot CONH_2$, is a colourless, sparingly soluble powder, which does not melt. The substitution of the group NH_2 for OEt in the above urethanes and in similar compounds causes a rise in the melting point of 60—80°; the difference increases with the molecular weight and melting point of the compounds compared.

J. B. T.

Alkylisocarbamides. By F. LENGFELD and J. STIEGLITZ (*Ber.*, **27**, 926—927).—When carbodiphenylimide, $C(NPh)_2$, is heated at 160—190° with anhydrous alcohol, it is converted into *ethylisodi-phenylcarbamide* (*ethylic phenylimidophenylcarbamate*),

$$NHPh \cdot C(NPh) \cdot OEt.$$
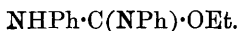
This substance, which is a colourless oil, resembling glycerol, boils at 200° under a pressure of 20 mm., and is readily soluble in the usual solvents. It combines with hydrogen chloride to form a salt, which decomposes at about 80°, ethylic chloride being evolved and carbani-lide left behind. Ethylisodiphenylcarbamide may also be obtained by treating the additive product of carbodiphenylimide and hydrogen chloride with sodium ethoxide. The investigation of these reactions is being continued. A. H.

Isomerism of Nitrobenzoic acids. By OECHSNER DE CONINCK (*Compt. rend.*, **115**, 538—540).—Ortho- and meta-nitrobenzoic acids are much more soluble than the para-derivative in dilute acetic acid, dilute hydrochloric acid, acetone, methylic alcohol, or ethylic alcohol. The para-derivative is only very slightly soluble in methylic and ethylic alcohols. (Compare this vol., i, 289.) C. H. B.

Separation of Phenyldibromobutyric acid into its Optically Active Constituents. By L. MEYER and O. STEIN (*Ber.*, **27**,

890—894).—Inactive phenyldibromobutyric acid is separated into its optically active constituents by crystallising the brucine salts from an alcoholic solution containing 1 mol. brucine to 2 mols. acid, or by employing molecular proportions of the base and acid and fractionally crystallising the salts from alcohol. The dextro-salt is the least soluble. The maximum rotations so far obtained are $[\alpha]_D = +88\cdot3°$ and $-54\cdot1°$. E. C. R.

Separation of Cinnamic Dibromide into its Optically Active Modifications. By R. HIRSCH (*Ber.*, **27**, 883—888).—Cinnamic acid dibromide cannot be resolved into its optically active modifications by means of inactive bases even if the solution of the salt is sown with crystals of the salt of the optically-active acid. Several optically active alkaloïdes can, however, be employed for this purpose. The salts of the acid with inactive bases are mostly well crystallised, and the following have been prepared. The *aniline salt*, $PhNH_2, C_9H_8Br_2O_2$, crystallises in needles and melts at 112°. The *neutral paratoluidine salt*, $C_6H_4Me\cdot NH_2,C_9H_8Br_2O_2$, forms microscopic crystals and melts at 130°. The *acid paratoluidine salt*, $C_6H_4Me\cdot NH_2,2C_9H_8Br_2O_2$, melts at 133°. The *quinoline salt* separates in large, transparent crystals, and melts at 118°. The *pyridine salt*, $C_5NH_5,2C_9H_8Br_2O_2$, crystallises in rhombs and melts at 138°. The *neutral piperidine salt* separates in measurable crystals and melts at 120° with decomposition. The *acid piperidine salt* separates in large measurable crystals and melts at 125°. The *α-naphthylamine salt* forms microscopic crystals and melts at 115°. The *β-naphthylamine salt* melts at 142°.

Cinchonine phenyl-αβ-dibromopropionate is obtained by mixing the base and acid in molecular proportions in absolute alcoholic solution. The precipitated salt yields an acid having the rotation $[\alpha]_D = -16\cdot1$.

Brucine phenyl-αβ-dibromopropionate.—When molecular proportions of the base and acid are mixed in a solution of absolute alcohol the precipitated salt yields an acid having the rotation $[\alpha]_D = +13\cdot5°$. If, however, 2 mols. of acid and 1 mol. of base are employed, the salt so obtained yields an acid having the rotation $[\alpha]_D = +21\cdot1°$; and if this salt is fractionally crystallised from absolute alcohol three times, the salt of the dextro-acid is obtained pure and yields an acid having the rotation $[\alpha]_D = +64°$. The salt crystallises in large, measurable crystals and melts at 88°.

Conchinine phenyl-αβ-dibromopropionate separates in large, colourless crystals and melts at 110°. Only a very partial separation is, however, obtained by this salt, and the acid of highest rotation obtained gave $[\alpha]_D = +9\cdot56°$.

Cinchonidine phenyl-αβ-dibromopropionate is prepared by mixing molecular proportions of the acid and base dissolved in benzene. The precipitated salt yields an acid having the rotation $[\alpha]_D = -14\cdot4°$. If this salt is extracted with benzene, converted into acid and then again converted into cinchonidine salt and the latter extracted again with benzene, a salt is obtained which yields an acid having the rotation $[\alpha]_D = -63\cdot6°$. The cinchonidine salt crystallises in slender needles and melts at 120°. E. C. R.

Optically-active Cinnamic Dichloride. By H. FINKENBEINER (*Ber.*, **27**, 889—890; compare Abstr., 1893, i, 415).—The author finds that cinnamic acid dichloride is most easily separated into its optically-active constituents by employing the strychnine and acid in molecular proportion, or with a slight excess of the acid. The maximum rotations obtained are $[\alpha]_D = + 66\cdot5°$ and $- 65\cdot9°$. No separation can be effected by means of optically inactive bases. Quinine, cinchonine, cinchonidine, narcotine, morphine, and cocaïne only afford a very partial separation.

Methylic and ethylic cinnamate dichloride are easily prepared by the usual methods. The methylic salt crystallises well, and melts at 100—101°; the ethylic salt is a liquid. When prepared from the inactive acid, they are inactive. The salts prepared from the dextro-acid have the rotations, for the methylic salt $[\alpha]_D = + 61\cdot9°$, for the ethylic salt $[\alpha]_D = + 64\cdot1°$. E. C. R.

Benzophenonoxime from Bisnitrosylbenzhydryl. By W. PLATNER and R. BEHREND (*Annalen*, **278**, 359—372).—When diphenylbromomethane is treated with alcoholic or aqueous hydroxylamine, non-nitrogenous products are formed; thus in the latter case benzhydrol ether $(C_{13}H_{11})_2O$ melting at 108°, is obtained (compare Friedel and Balsohn, Abstr., 1880, 558). *α-Benzyl-β-benzhydrylhydroxylamine*, $CHPh_2\cdot NH\cdot O\cdot CH_2Ph$, is obtained by warming finely pulverised diphenylbromomethane with benzylhydroxylamine (2 mols.). The *hydrochloride* crystallises in rosettes of white needles, and melts at 193—194°·5. Attempts failed to effect the removal of the benzyl group by treatment with hydrochloric acid.

When diphenylbromomethane is boiled with acetoxime and acetic acid, *β-benzhydrylhydroxylamine hydrobromide*, $CHPh_2\cdot NH\cdot OH,HBr$, is obtained; it is purified by conversion into the *oxalate*, which forms small white needles and melts at 171°. The *hydrochloride* melts at 172°. The free *base* crystallises in small, flat prisms, is readily soluble in water, reduces Fehling's solution, and melts at 78°. *Nitroso-β-benzhydrylhydroxylamine*, $CHPh_2\cdot N(OH)\cdot NO$, is formed when the hydrochloride of the last-described base is treated with sodium nitrite; it melts at 84—85°, and does not give Liebermann's reaction. If the nitroso-derivative is dissolved in ether and a few drops of concentrated hydrochloric acid added to the solution *bisnitrosylbenzhydryl*, $N_2O_2(CHPh_2)_2$, is obtained together with benzhydrol ether (m. p. 108°). The former crystallises in white needles, melts at 118—120°, does not give Liebermann's reaction, and is sparingly soluble in all solvents except chloroform. Aqueous alkalis have no action on the compound, but alcoholic alkalis slowly dissolve it, forming benzophenonoxime (m.p. 140°). A. R. L.

Constitution of Triphenylmethane Dyes. By A. ROSENSTIEHL (*J. pr. Chem.*, [2], **49**, 317).—With reference to Stock's statement (*J. pr. Chem.*, [2], **47**, 403; Abstr., 1893, i, 472) that Hofmann first proposed that these dyes should be regarded as ethereal salts of amido-aromatic alcohols, the author states that he was the first to make this suggestion (Abstr., 1880, 553). A. G. B.

Aurin. By J. HERZIG and T. v. SMOLUCHOWSKI *(Monatsh.*, **15.** 73—84; compare Abstr., 1892, 1319).—The acetyl-derivative of aurin, first prepared by Graebe and Caro (Abstr., 1878, 794), is found, when perfectly pure, to melt at 171—172°, and to have the formula $C_{19}H_{13}O_4Ac_3$, and not $C_{19}H_{14}O_3 + Ac_2O$, that previously ascribed to it. The compound must, therefore, be regarded not as a derivative of aurin, but of a substance having the formula $C_{19}H_{16}O_4$. On hydrolysis, however, it is readily converted into aurin, $C_{19}H_{14}O_3$. Acetylaurin is readily reduced to triacetylleucaurin, and, consequently, contains three acetyl-groups occupying the same position as those in the last-named compound. The authors have not succeeded in recognising the presence of a free hydroxyl-group in acetylaurin.

G. T. M.

Derivatives of Naphthyl Ethyl Ether. By C. DUISBERG *(J. pr. Chem.*, [2], **49**, 320).—Heermann (this vol., i, 251) is in error in supposing that the dye-stuffs which he has prepared and referred to in his paper on the above subject, are new; they form the claims in recent patents.

A. G. B.

2 : 3-Naphthylenediamine. By P. FRIEDLÄNDER and S. v. ZAKRZEWSKI *(Ber.*, **27**, 761—765).—When 2-naphthol-3 : 3'-disulphonic acid (Abstr., 1889, 515) is fused with caustic soda at 220°, 2 : 3-dihydroxynaphthalene-3'-sulphonic acid is formed, and this, when heated at 180—190° with dilute sulphuric acid, yields 2 : 3-*dihydroxynaphthalene*, which crystallises in colourless, rhombic plates, melts at 159°, yields no quinone when oxidised, but with 1 mol. of a diazo-compound, and with greater difficulty with 2, gives a dark azo-dye.

2 : 3-Amidonaphthol·3'-sulphonic acid yields dihydroxynaphthalene when heated at 180—200° with dilute acid. If the latter compound is heated with concentrated ammonia at 135—140°, 2 : 3-*amidonaphthol* is formed; it crystallises in small, brownish needles, melts at 234°, and yields a *diacetyl-derivative*. If the heating is done at 240°, 2 : 3-*naphthylenediamine* is formed; this crystallises in greyish plates, melts at 191°, and yields a red azo-dye with 1 mol. of a diazocompound. Its *diacetyl-derivative*, $C_{10}H_6(NHAc)_2$, crystallises in brownish needles melting at 247°, and, when boiled with glacial acetic acid, yields an anhydride, $C_{10}H_6{<}{\stackrel{-N}{NH}}{>}CMe$, which crystallises in white needles, and melts at 168°. Moreover, with nitrous acid, 2 : 3-naphthylenediamine yields an *azimide*, $C_{10}H_6{:}N_3H$, which crystallises in yellowish needles, melting at 187°; with dihydroxytartaric acid, *naphthyl-2 : 3-quinoxalineorthodicarboxylic acid*, $C_{12}H_5N_2(COOH)_2$, is formed in yellow needles melting at 192°, whilst, with oxalic acid, it yields white crystals of *dihydroxynaphthylquinoxaline*, $C_{12}H_6N_2(OH)_2$, melting above 350°.

C. F. B.

Chrysene and Chrysofluorene. By C. GRAEBE *(Ber.*, **27**, 952—955).—*Isochrysofluorene* (1 : 2- or 1 : 1'-naphthylenephenylenemethane) is prepared by passing the vapour of α-benzylnaphthalene through a red-hot tube, and is purified by means of the picrate. It is crystalline, and melts at 76°. The presence of chrysofluorene could not be

detected. The *picrate* is yellowish-red, and melts at 122·5°. On oxidation, the hydrocarbon yields a ketone, $CO < {}^{C_{10}H_6}_{C_6H_4}$, which is red, and has a low melting point. β-Benzylnaphthalene (free from the α-compound) is converted at high temperatures into chrysofluorene; this melted at 186—187°, and was further identified by oxidation to chrysoketone. The author's previous observation of the formation of β-phenylnaphthalene, by heating chrysoquinone with soda-lime under the ordinary pressure, is confirmed.

J. B. T.

Cycloïd Ketoximes. Conversion of Terpene Derivatives into Aliphatic Compounds containing the same Number of Carbon Atoms. By O. WALLACH (*Annalen*, **278**, 302—329).—It has been already shown (this vol., i, 46) that cycloïd ketoximes undergo isomeric change when treated with phosphorus pentachloride. It is now found that the same change may be readily effected by concentrated sulphuric acid. The nitriles formed by the action of dehydrating agents on cycloïd ketoximes (*loc. cit.*) are, without doubt, aliphatic compounds; they appear to be closely related to the odoriferous substances occurring in natural ethereal oils.

When l-menthonoxime (m. p. 59°) is dropped into concentrated sulphuric acid cooled by ice, it is converted into the isomeride melting at 119—120° (*loc. cit.*). If the latter is dissolved in chloroform and treated with phosphorus pentachloride (1 mol.), hydrogen chloride is evolved, and when the product is mixed with water the oxime is regenerated. When, however, the solvent is distilled off under diminished pressure at a low temperature, a strong bivalent *base*, $C_{20}H_{35}ClN_2$, is obtained; this crystallises from alcohol in transparent prisms, melts at 59—60°, and probably has the constitution
$$\begin{matrix} CH_2 \cdot CHPr^\beta \cdot C:N \cdot CH \cdot CHMe \cdot CH_2 \\ | \qquad\qquad\qquad\qquad\qquad | \\ CHCl \cdot CHMe \cdot CH_2 \quad CH_2 \cdot CHPr^\beta \cdot C:NH \end{matrix}.$$ Its specific rotatory power in alcohol is $[\alpha]_D = -186·35$. Several crystalline salts are described. From the formation of this base, it follows that the isomeride of menthonoxime melting at 119—120°, is not an oxime; probably it has the constitution $CHPr^\beta < {}^{CH_2 \cdot CH(OH)}_{C(NH) \cdot CH_2} > CHMe$.

In the preparation of the nitrile from menthonoxime and phosphoric anhydride (*loc. cit.*), it is best to use an indifferent diluent; but the nitrile is more readily obtained by treating a chloroform solution of the compound melting at 119—120° (mentioned above) with phosphorus pentachloride; it is also formed when menthonoxime is boiled for a long time. Mentho-nitrile boils at 225—226°, has a sp. gr. at 20° = 0·8355, a specific refractive power $[n]_D = 1·4445$ at 20°; its constitution is probably $CHMe_2 \cdot CH(CN) \cdot CH_2 \cdot CH_2 \cdot CMe:CH_2$. The *amide*, $C_9H_{17} \cdot CONH_2$, is formed by boiling the nitrile for half an hour with alcoholic soda; it crystallises in satiny plates, and melts at 105—106°. By prolonging the treatment of the nitrile with alcoholic soda, the *acid* $C_9H_{17} \cdot COOH$ is obtained; it forms a sparingly soluble silver salt.

When the nitrile is reduced with sodium and alcohol two bases are

formed which may be separated by means of their oxalates. The first *base, aliphatic menthylamine* (menthonylamine), $C_{10}H_{19}\cdot NH_2$, forms a sparingly soluble *oxalate*. The free base boils at 207—208°, and closely resembles the cycloid menthylamines in odour; its sp. gr. at 20° is 0·8075, and its specific refractive power at 20° is $\lfloor n \rfloor_D =$ + 1·45 ; it is feebly dextrorotatory. Several *salts* as well as a liquid *acetyl*-derivative and an *oxamide* melting at 82—83°, were prepared. The second *base* obtained by the reduction of the nitrile has the formula $C_{10}H_{23}NO$; it boils at 252—253°.

If menthonylamine nitrite is boiled with water, an alcohol and a hydrocarbon are obtained. The alcohol, $C_{10}H_{19}\cdot OH$, is a colourless liquid resembling linalool, and has all the properties of a primary aliphatic alcohol ; it boils at 95—105° under a pressure of 7 mm., has a sp. gr. at 20° = 0·8315, a specific refractive power at 20° $[n]_D =$ 1·44809, and a specific rotatory power $[\alpha]_D = +2$. The *hydrocarbon*, $C_{10}H_{18}$, boils at 153—156°, and has sp. gr. = 1·4345 at 15°. When the last-mentioned alcohol is oxidised with chromic acid, an aldehyde, $C_{10}H_{18}O$, is obtained which is distinguished from the natural products citral, linalool, and geraniol by its intense orange-like odour. A complete comparison of this aldehyde with that from orange-oil has not yet been made. The paper concludes with a lengthy theoretical discussion of these results.　　　　　　　　　　　　A. R. L.

Isomeric Methylcyanocamphors. By A. HALLER and MINGUIN (*Compt. rend.*, 118, 690—693).—When crude methylcyanocamphor is kept below 0° for some time, crystals are deposited, and can be purified by recrystallisation from a mixture of ether and light petroleum. They are insoluble in water and alkalis, but dissolve in alcohol or ether, melt at 63°, and have a molecular rotatory power $[\alpha]_D =$ +150·8°. The crystals have the composition of methylcyanocamphor, and with aqueous hydrochloric acid decompose quantitatively into methylic chloride and cyanocamphor, the latter being soluble in potassium hydroxide. With bromine, the compound yields methylic bromide and a bromocyanocamphor identical with that obtained by the action of bromine on cyanocamphor in presence of carbon bisulphide. Potassium hydroxide in time converts it into hydroxycamphocarboxylic acid, identical with that obtained by the action of the alkali on cyanocamphor, methylic alcohol being, doubtless, formed at the same time.

This modification of methylcyanocamphor, which the authors distinguish as the β-modification, has, in all probability, the constitution $C_8H_{14} \begin{cases} C\cdot CN \\ \| \\ C\cdot OMe \end{cases}$·

The liquid portion has the same composition as the crystals, and can be freed from the last traces of the latter by treatment with hydrochloric acid followed by potassium hydroxide. The purified product, which the authors distinguish as α-methylcyanocamphor, is a thick, yellowish liquid with a rotatory power $[\alpha]_D = +90\cdot1°$. Sometimes it deposits soft, yellow crystals which melt at 38—45°, and have the same composition and rotatory power as the liquid. Hydrochloric acid has no action on this compound in the cold.

When boiled with alcoholic potash, it yields ammonia and methyl-hydroxycamphocarboxylic acid, which melts at 175°, and has a rotatory power $[\alpha]_D = +26\cdot31°$. It would seem, therefore, that the α-modification has the constitution $C_8H_{14}{<}^{CMe\cdot CN}_{CO}$. Schutzenberger has supposed that a radicle displacing the hydrogen in cyanocamphor can attach itself either to the $\vdots$C·CN group or the $\vdots$CO group according to the conditions.

Other alkylic iodides and chlorides act on sodiocyanocamphor, in the same way that methylic iodide does, and it is noteworthy that the higher homologues of methylic iodide yield very small quantities of the α-modifications.

The behaviour of the cyanocamphors affords further evidence that in many compounds the molecular arrangement is unstable and is liable to partial changes in a manner which is not represented by the ordinary constitutional formulæ. C. H. B.

Camphoric acid. By W. A. NOYES (*Ber.*, **27**, 917—919).— *Methylic camphoramate*, $NH_2\cdot CO\cdot C_8H_{14}\cdot COOMe$, is obtained by treating methylic camphorate with phosphorus oxychloride and ammonia. It crystallises in white needles, and melts at 152—153°. The *chloride* crystallises in transparent tablets, and melts and decomposes at 244°.

β-*Camphoramic acid* is obtained by heating camphoricimide with 10 per cent. sodium hydroxide solution. It crystallises in lustrous prisms, melts at 182—183°, and is different from Claisen and Manasse's acid (*Annalen*, **274**, 81).

Dihydroaminocampholytic acid is obtained by heating camphoricimide with aqueous soda, and then warming the mixture with bromine. It crystallises in granules or in nacreous plates, and sublimes without melting. E. C. R.

Tanacetone and its relation to Thujone. By F. W. SEMMLER (*Ber.*, **27**, 895—898; compare Abstr., 1893, i, 107).—Tanacetone, $^{CHPr\cdot CH\cdot CO}_{CH_2-CH\cdot CHMe}$ (b. p. 203°), when heated at 280° for 24 hours in a sealed tube, is converted into a product which boils at 220—235°, and, when treated with hydroxylamine, yields an *oxime*, which melts at 92—93°. This oxime, when warmed with dilute sulphuric acid, yields pure *carvotanacetone*, $CPr{<}^{CH\cdot C(OH)}_{CH_2-CH_2}{>}CMe$. This boils at 228°, and has the sp. gr. $= 0\cdot9373$ at 17°, $[n]_D = 1\cdot4835$. It has an odour closely resembling that of carvone.

Tetrahydrocarvotanacetone, $C_{10}H_{20}O$, obtained by reducing carvotanacetone with sodium and alcohol, boils at 219—220°, has a sp. gr. of $0\cdot9014$ at 17°, and $[n]_D = 1\cdot4685$. It has an odour resembling that of terpineol, and, in properties, closely resembles hexahydro-oxy-cymene, obtained by Wallach from terpineol.

Both tanacetone and absinthone, which the author believes are identical, combine with sodium hydrogen sulphite, and yield solid

oximes; whereas thujone and salvone do not, and they also differ from tanacetone in physical properties.　　　　　　　　E. C. R.

Synthesis of Gentisin. By S. v. KOSTANECKI and J. TAMBOR (*Monatsh.*, **15**, 1—8; compare Abstr., 1891, 1244, and 1386).—When gentisinic acid (hydroquinonecarboxylic acid, $C_6H_3(OH)_2 \cdot COOH$ and phloroglucinol are mixed in molecular proportion, and, after adding acetic anhydride, the mixture is distilled in small retorts, a small quantity of gentiseïn, $C_{13}H_8O_5$, is obtained as a sublimate in the neck of the retort; it forms yellow needles. This synthesis, taken in conjunction with previous observations (*loc. cit.*) indicates that gentiseïn is the 1 : 3 : 7-trihydroxyxanthone,

$$OH \cdot C_6H_3 <^{O}_{CO}> C_6H_2(OH)_2.$$
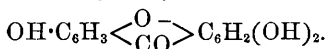
The *methyl ether* of *gentiseïn* is readily obtained on treating that substance with methylic iodide and potassium hydroxide, and proves to be identical with natural gentisin, $C_{13}H_7O_4 \cdot OMe$.

Dibenzoylgentisin, $C_{14}H_8O_5Bz_2$, whether obtained from the natural or synthetical product, was found to crystallise from alcohol in thick, white needles, and to melt at 192°. The monobenzoyl derivative of gentisin methyl ether, $C_{13}H_5O_2(OMe)_2 \cdot OBz$, crystallises in white, gleaming masses of needles, and melts at 197°.　　　　　G. T. M.

Isolation of Sugars from Glucosides. By E. SCHUNCK and L. MARSCHLEWSKI (*Annalen*, **278**, 349—359).—The authors confirm their previous statement (this vol., i, 142) that the sugar obtained by hydrolysing datiscin is rhamnose. The sugar formed by hydrolysing lupinin (Schulze and Barbieri, *Ber.*, **11**, 2220) gives an osazone melting at 204°, identical with ordinary glucosazone. Inasmuch as lupinin sugar is dextro-rotatory and fermentable (*loc. cit.*), the authors consider the proof that it is identical with ordinary glucose to be complete. Rochleder and Schwarz (*Annalen*, **30**, 200) consider that æsculin, on hydrolysis, yields a sugar which is not identical with glucose. The authors have prepared the osazone from this sugar; it melts at 205—206°, and in all its other properties is identical with glucosazone. The same remarks apply to the sugars from rubiadin and arbutin; in the latter case, the melting points of the sugar itself (hydrated and anhydrous) are shown to be the same as those of glucose. The authors likewise prove conclusively that the sugar from phloridzin is ordinary glucose. The view recently advanced by Hesse (this vol., i, 104) that the freshly prepared sugar is subsequently converted into glucose perhaps through the agency of micro-organisms, is negatived by the fact that the sugar prepared by the authors was kept sterilised, and it was found to be identical with glucose a fortnight after its preparation. The authors have prepared the sugar from crocetin, and converted it into the osazone; this was homogeneous, and had the properties of glucosazone. The sugar from picrocrocin also gave glucosazone.　　　　　　　A. R. L.

Action of Bromine on Datiscetin. By E. SCHUNCK and L. MARCHLEWSKI (*Annalen*, **278**, 346—349).—When datiscetin (this

vol., i, 143) is dissolved in glacial acetic acid and treated with a small quantity of bromine, salicylic acid and bromosalicylic acid are formed; if an excess of bromine is used and the liquid is boiled, bromanil separates on cooling, whilst tribromophenol remains dissolved in the mother liquor. That salicylic acid is the initial product in the latter case is proved by the fact that this acid is readily converted into bromanil and tribromophenol when boiled with bromine in glacial acetic acid solution, and it is incidentally mentioned that this is a convenient and rapid method of preparing bromanil.

A. R. L.

Brasilin and Hæmatoxylin. By J. HERZIG (*Monatsh.*, 15, 139—146; compare Abstr., 1893, i, 426).—The author finds that the amorphous product obtained by the interaction of trimethylbrasilin, acetic anhydride, and sodium acetate gradually becomes crystalline after long exposure to the air. The substance, when deposited from alcoholic solution, forms beautiful, compact crystals, which melt at 172—174° (uncorr.), and, on analysis, prove to be *acetyltrimethylbrasilin*, $C_{16}H_{10}O_5Me_3Ac$. *Tetramethylbrasilin*, $C_{16}H_{10}O_5Me$, is readily obtained on heating trimethylbrasilin, potassium hydroxide, and methylic iodide in a water bath for 7—8 hours. It is only sparingly soluble in cold alcohol, from which it crystallises in beautiful, white scales, and melts at 137—138°. Both trimethylbrasilin and tetramethylbrasilin are decomposed by alcoholic potash at 150—160°, yielding products soluble in potash.

On methylation, hæmatoxylin behaves similarly to brasilin. *Tetramethylhæmatoxylin*, $C_{16}H_{10}O_6Me_4$, crystallises from alcohol in slender needles, melts at 139—140°, and, on treatment with acetic anhydride and sodium acetate, gives rise to *acetyltetramethylhæmatoxylin*, $C_{16}H_9O_6Me_4Ac$, which crystallises in beautiful, white needles, and melts at 178—180°. *Pentamethylhæmatoxylin*, $C_{16}H_9O_6Me_5$, is prepared from the tetramethyl derivative by a method corresponding with that used for obtaining tetramethylbrasilin from trimethylbrasilin, and melts at 144—147°.

The observation that all the hydroxyl groups in brasilin and hæmatoxylin do not behave similarly on methylation appears to indicate that in all probability those substances are constituted similarly to xanthone and fluoran.

G. T. M.

Chlorophyll. By E. SCHUNCK and L. MARCHLEWSKI (*Annalen*, 278, 329—345).—According to the authors' experiments, the action of hydrochloric acid on an alcoholic solution of chlorophyll appears to proceed as follows. The chlorophyll is first converted into chlorophyllan (Hoppe-Seyler, *Zeit. physiol. Chem.*, [3], 5; Tschirsch, *Unters. über Chlorophyll*, 1884), and thence into an amorphous substance, phylloxanthin, which is then transformed into fatty acids (?), and a crystalline compound, phyllocyanin. Both phylloxanthin and phyllocyanin form crystalline compounds with copper acetate; that obtained from phyllocyanin gave analytical values indicating the possible empirical formula $C_{68}H_{71}N_5O_{17}Cu_2$. When phyllocyanin is evaporated with hydrochloric acid or treated with alkalis, phyllotaonin is obtained.

Hansen believes (*Die Farbstoffe d. Chlorophyll*, 1889) that the treatment of chlorophyll with alkalis consists in the removal of the combined fatty acids by hydrolysis, the colouring matter itself remaining intact. He contends that after such treatment the colouring matter is much purer than before. The authors have observed, however, considerable differences in the absorption spectra of chlorophyll solutions before and after treatment with alkalis, which they consider to be incompatible with Hansen's views (see also below).

When grass is boiled with alcoholic soda, and hydrogen chloride is passed through the filtrate, stellate groups of brown needles having a purple reflex separate, together with sodium chloride. If, after purification, this substance is crystallised from methylic or ethylic alcohol, *methylphyllotaonin* and *ethylphyllotaonin* are obtained respectively. The methyl derivative melts at about 210°; its greenish-blue solution in concentrated hydrochloric acid exhibits the absorption spectrum observed with phyllocyanin in the same solvent. *Phyllotaonin* is obtained by treating either of the last-described compounds with alcoholic alkali; it has acidic properties. It crystallises from ether in opaque scales having a steel-blue reflex. Analyses of phyllotaonin and of its methyl and ethyl derivatives agree with the formulæ $C_{40}H_{38}N_6O_5 \cdot OH$, $C_{40}H_{38}N_6O_5 \cdot OMe$, and $C_{40}H_{38}N_6O_5 \cdot OEt$ respectively. When phyllotaonin is boiled with glacial acetic acid, an *acetyl* derivative is obtained which gave analytical values in agreement with the formula $C_{40}H_{38}N_6O_5 \cdot OAc$. A. R. L.

α-**Epichlorhydrinpiperidine Derivatives.** By L. NIEMILOWICZ (*Monatsh.*, **15**, 118—131).—When piperidine is shaken with an equivalent quantity of *α*-epichlorhydrin, suspended in 10 times its weight of water, a milky liquid is formed, from which ether extracts a base, characterised by the formation of the following salts. The *hydrochloride* crystallises in prisms, and melts at 156·5°; the *platinochloride*, $(C_8H_{16}NOCl)_2, H_2PtCl_6$, crystallises in yellow prisms, which are only sparingly soluble in water. The base is 1-*chlorhydrinpiperidine*, $C_8H_{16}NOCl$, a colourless oil, which decomposes on distillation at ordinary pressures, and on treatment with sodium hydroxide, in anhydrous ethereal solution, gives rise to a new base, *α-epipiperidinehydrin*, $C_8H_{15}NO$. The latter boils without decomposition at 198° (uncorr.), and if left with dilute hydrochloric acid for some time, is converted into 2-*chlorhydrinpiperidine*, which differs from its stereoisomeride, described above, in forming a *platinochloride*, much more soluble in water, and crystallising in golden-yellow scales. Both platinochlorides, however. melt at 189°, with slight decomposition. On evaporating an ethereal solution of 1-chlorhydrinpiperidine, white, cholesterol-like crystals of *piperidiniumhydrin chloride* are obtained. This is insoluble in ether, but dissolves readily in water, yields a characteristic platinochloride, $(C_8H_{16}ONCl)_2PtCl_4$, and when gently heated with dilute aqueous sodium hydroxide, is converted into the isomeric epipiperidinehydrin. When piperidiniumhydrin chloride is heated, either dry, or in aqueous solution, it forms a vitreous, non-crystalline substance, *piperiliumhydrine chloride*, which yields an amorphous platinochloride, $(C_8H_{16}NOCl)_2PtCl_4$. *α*-Epichlorhydrin and excess of piperidine

give rise to the formation of symmetrical *dipiperidinehydrin*, $C_{13}H_{26}N_2O$, which distils unchanged at 288° (546 mm.), melts at 11—12°, and forms a platinochloride, $C_{13}H_{26}N_2O,H_2PtCl_6$, crystallising in pyramids or scales. The same base is formed from symmetrical, as well as from unsymmetrical, dichlorhydrin.

<div align="right">G. T. M.</div>

Decomposition of α-Hydroxynicotinic acid with Nascent Hydrogen. By T. v. SMOLUCHOWSKI (*Monatsh.*, **15**, 55—71).—By the action of sodium amalgam on the pyridine-monocarboxylic and -dicarboxylic acids (compare Abstr., 1891, i, 114), the group —CH:N·CH: was resolved eventually into —CO·O·CH₂—, and non-nitrogenous acids thereby formed. The author has determined the effect of the reducing agent on a hydroxypyridinecarboxylic acid, namely, α-hydroxynicotinic acid, and finds that in this case the reduction does not occur in so simple a manner, the products varying according to the alkalinity and degree of concentration of the solution. The following substances were isolated in a pure state. *Iso-α-methylglutaconic acid*, $C_6H_8O_4$. This crystallises in monosymmetric prisms, $a : b : c = 0·8360 : 1 : 0·4558$. It is readily soluble in water, melts at 141°, and has the constitution

$$COOH·C(CH_2)·CH_2·CH_2·COOH,$$
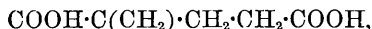
or more probably COOH·CMe:CH·CH₂·COOH. It forms the micro-crystalline salts, $C_6H_6O_4Ba$, and $C_6H_6O_4Ag_2$, and the dibromide, $C_6H_8O_4Br_2$, which dissolves readily in water, alcohol, and ether, and melts and decomposes at 160°. On further reduction with hydriodic acid, it forms α-methylglutaric acid, which melts at 77°. *Iso-α-methylglutaconamide*, $C_6H_9O_3N + H_2O$, crystallises from water in scales, and melts at 182—183° (uncorr.). In addition to these crystalline substances, a syrupy brown liquid was obtained, but this refused to crystallise, even after being kept for several months, and the author has been unable to determine its nature. The formation of iso-α-glutaconic acid in the reaction is in all probability the result of a secondary change, as it is scarcely conceivable that an unsaturated acid could be formed in a solution from which hydrogen was being evolved.

<div align="right">G. T. M.</div>

Halogen Alkyl Derivatives of Isoquinoline. By A. CLAUS (*J. pr. Chem.*, [2], **49**, 295—307).—Attention has already been called to the existence in the cinchona alkaloïd of a nitrogen atom whose function is similar to that of the nitrogen atom in isoquinoline (Abstr., 1892, 1249). The alkylene bases, also previously described (Abstr., 1892, 1358), must be regarded as having their alkylene groups centrally disposed within the nitrogen ring.

It is shown that the similar derivatives of the cinchona alkaloïds probably have an analogous structure, for the decomposition of isoquinoline and of these alkaloïds when heated with an alkylic iodide and potassium hydroxide, is of the same deep-seated character, and is attended by the formation of similar products.

Methylene-isoquinoline has been isolated in an impure condition as a

viscid liquid by the action of potassium hydroxide on isoquinoline methiodide; its *methiodide*, $C_9NH_7(CH_2),MeI$, has also been isolated in an impure condition.

Isoquinoline methyldichromate, $C_9NH_7,MeCr_2O_7$, is an orange-yellow, crystalline precipitate, thrown down from the aqueous solution of isoquinoline methiodide by potassium dichromate; it decomposes at 218°.

Methylene-isoquinoline methochloride platinochloride,

$$[C_9NH_7(CH_2),MeCl]_2,PtCl_4,$$
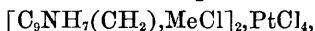
is a yellow, crystalline, anhydrous powder, and decomposes at 230°.

Bismethyleneisoquinoline is the product of the treatment of methyl-eneisoquinoline methiodide with potassium hydroxide; it is a viscid, insoluble liquid, and readily forms a *methiodide*, which, however, cannot be made the means of introducing another methylene group into the isoquinoline. A. G. B.

4′-Parahydroxyphenylquinoline. By E. BESTHORN and G. JAEGLÉ (*Ber.*, **27**, 907—914).—The authors have prepared 4′-para-hydroxyphenylquinoline synthetically from methoxyacetophenone by the method of Claisen and Beyer (*Ber.*, **20**, 2178).

Paramethoxybenzoylacetone, $OMe \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot COMe$, is obtained from paramethoxyacetophenone by the action of ethylic acetate and sodium methoxide. It forms beautiful, white crystals, and melts at 54·5°. The *anilide* forms beautiful, bright-yellow crystals, and melts at 111—112°.

4′-Paramethoxyphenylquinaldinesulphonic acid is obtained when the above anilide is treated with concentrated sulphuric acid. It is separated by means of its *barium salt*, $C_{34}H_{28}N_2S_2O_8Ba,10H_2O$, which crystallises in white needles. The pure acid crystallises in slender, white needles, and when boiled with concentrated hydrobromic acid is converted into 4′-parahydroxyphenylquinaldine hydrobromide. When the above barium salt is heated with benzaldehyde and zinc chloride at 160°, a *benzylidine compound* is obtained.

4′-Parahydroxyphenylquinaldinic acid, $OH \cdot C_6H_4 \cdot C_9NH_5 \cdot COOH$, is obtained by oxidising the preceding benzylidene compound with potassium permanganate, and then heating the sulphonic acid so obtained with concentrated hydrobromic acid; it crystallises in yellow needles, melts at 234—235° with evolution of carbonic anhydride, and, when heated with acetic anhydride, yields a beautiful, red dye.

4′-Parahydroxyphenylquinoline is obtained by heating the preceding acid at 250°. It melts at 243°, and is identical with the phenolquinoline obtained by Königs and Nef (*Ber.*, **20**, 629) from apocinchene. E. C. R.

5-Methylpyrazole. By R. v. ROTHENBURG (*Ber.*, **27**, 955—956). —Methylpyrazole, $CMe{<}^{NH \cdot N}_{CH \cdot CH}$, is prepared by the action of hydrazine acetate on sodium acetoacetaldehyde, and has been previously described by G. Marchetti (*Abstr.*, 1893, i, 179). It does not combine with benzaldehyde, and yields no azo-derivative. The

hydrochloride and *sulphate* are readily soluble. 5-*Pyrazolecarboxylic acid*, $COOH \cdot C \begin{smallmatrix} NH \cdot N \\ \| \\ CH \cdot CH \end{smallmatrix}$, is formed by the oxidation of 5-methyl-pyrazole with potassium permanganate, and is deposited in granular crystals melting at 215—216°. The *silver salt* decomposes on exposure to light, and, like the acid, yields pyrazole on distillation.

5-*Methylpyrazoline*, $CHMe \begin{smallmatrix} NH \cdot N \\ \| \\ CH_2 \cdot CH \end{smallmatrix}$, is prepared by the action of crotonaldehyde on hydrazine hydrate; it is a yellowish oil with a characteristic odour; it boils and partly decomposes at 180°. It yields an oily methylpyrazole on careful oxidation.　　　J. B. T.

The Pyrazole Series. By L. CLAISEN (*Annalen*, **278**, 261—273). —Introductory remarks and theoretical considerations on the paper following (next abstract). The fact that 5 : 1-methylphenylpyrazole, obtained from hydroxymethylenacetone, is identical with that prepared in other ways, seems to furnish evidence that isomeric phenyl-pyrazoles having one or more diagonal bonds—analogous to the isindazoles of Fischer and Tafel (*Annalen*, **227**, 303)—do not exist.
　　　　　　　　　　　　　　　　　　　　　　　　　　A. R. L.

Action of Phenylhydrazine on Hydroxymethyleneacetone and on Acetoneoxalic acid. By L. CLAISEN and P. ROOSEN (*Annalen*, **278**, 274—296; compare Abstr., 1891, 1106).—The authors have now definitely proved that the product of the action of phenyl-hydrazine on the sodium compound of hydroxymethyleneacetone (acetoacetaldehyde) is a mixture of 5 : 1-methylphenylpyrazole (2 parts) and 3 : 1-methylphenylpyrazole (1 part). When this mixture is cooled, the latter compound crystallises out; it melts at 37°, and boils at 254—255° under a pressure of 720 mm. (compare Claisen and Stylos, Abstr., 1888, 671; Knorr, *Annalen*, **225**, 202; Andreocci, *Atti Acad. Lincei*, 1891, i, 269; ii, 157).

1-*Phenylpyrazole-3-carboxylic acid*, $NPh \begin{smallmatrix} N = C \cdot COOH \\ \\ CH : CH \end{smallmatrix}$, is obtained by oxidising 3 : 1-methylphenylpyrazole with alkaline permanganate; it crystallises in silky needles, and melts at 146°; the *methylic* salt melts at 77°.

The compound obtained from phenylhydrazine and ethylic sodacetoneoxalate (acetopyruvate) is 5 : 1-methylphenylpyrazole-3-carboxylic acid, $NPh \begin{smallmatrix} N = C \cdot COOH \\ \\ CMe : CH \end{smallmatrix}$; its properties have been already described (*loc. cit.*). The *phenylazo*-derivative, $NPh \begin{smallmatrix} N = C \cdot COOH, \\ \\ CMe \cdot C \cdot N_2Ph \end{smallmatrix}$ prepared by the successive action of diazobenzene chloride and phenylhydrazine on acetoneoxalic acid, crystallises from hot alcohol in yellow, satiny needles, and melts at 206—207° with evolution of gas.

1-Phenyl-3 : 5-dicarboxylic acid (see *loc. cit.*).

5 : 1-Methylphenylpyrazole was prepared in large quantity by distilling 5 : 1-methylphenylpyrazole-3-carboxylic acid. The authors

find that the pure compound boils at 254—255° (720 mm.), has a sp. gr. at 15° of 1·085, and cannot be solidified when cooled. The platinochloride, when air dried, contains water of crystallisation and melts at 149°; after being heated at 100°, it is rendered anhydrous, and then melts at 171° with decomposition; the methiodide melts at 296° and the ethiodide at 208°. 5 : 1-Phenylpyrazolecarboxylic acid is obtained by oxidising 5 : 1-methylphenylpyrazole with alkaline permanganate; it crystallises in short, white needles and melts at 183°. The *methylic* salt melts at 67°.

3 : 1-*Methylphenylpyrazole-5-carboxylic acid* is formed in small quantity as a bye-product by the interaction of phenylhydrazine and acetonoxalic acid; it crystallises in feathery groups of needles, melts at 189—190°, and, when heated, decomposes into 3 : 1-methylphenyl-pyrazole; the *methylic* salt melts at 65—66°, and the *amide* melts at 181°.

Dimethyldiphenyldipyrazole, $NPh<\substack{N = C-C = N \\ CMe:CH \ CH:CMe}>NPh$, is obtained by the action of phenylhydrazine on a solution of oxalyldiacetone in glacial acetic acid; it forms colourless needles, and melts at 142°. The corresponding *tetraphenyl*-derivative, formed by the interaction of phenylhydrazine and oxalyldiacetophenone, melts at 232°. A. R. L.

Sulphophenyl- and Hydroxyphenyl-pyrazoles.

By L. CLAISEN and P. ROOSEN (*Annalen*, **278**, 296—302).—Paraphenyldimethyl-pyrazolesulphonic acid (Abstr., 1891, 1107) crystallises in rhombic hemimorphic prisms, $a : b : c = 0·5558 : 1 : 0·7889$, containing 1 mol. H_2O. *Parahydroxyphenyl*-3 : 5-*dimethylpyrazole* is obtained by fusing the sulphonic acid with potash; it crystallises from hot water in long needles, melting at 166°; the acetyl-derivative melts at 69°. *Paraphenylmethylphenylpyrazolesulphonic acid*,

$$C_3N_2HMePh·C_6H_4·SO_3H,$$
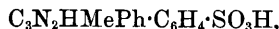
is obtained by the interaction of benzoylacetone and phenylhydr-azineparasulphonic acid; it crystallises from water in colourless, anhydrous prisms, and yields the *hydroxy*-derivative,

$$C_3N_2HMePh·C_6H_4·OH,$$

when fused with potash. The latter crystallises in rhombohedra, melts at 206°, and its *acetyl*-derivative at 133°. *Paraphenylmethyl-pyrazolesulphonic acid*, $C_3N_2H·Me·C_6H_4·SO_2H$, prepared from the sodium-derivative of hydroxymethylenacetone and phenylhydrazine-sulphonic acid, forms yellowish prisms. A. R. L.

Action of Ethereal Diazoacetates on Ethereal Salts of Unsaturated acids.

By E. BUCHNER and H. WITTER (*Ber.*, **27**, 868—876; see also Abstr., 1893, i, 429).—*Methylic pyrazoline*-3 : 4 : 5-*tri-carboxyacetate*, $NH<\substack{CH(COOMe)·C(COOMe)·CH_2COOMe \\ N = C·COOME}$, is obtained by heating methylic aconitate with methylic diazoacetate in

a reflux apparatus at about 60°, and then completing the action by heating in a water bath. It melts at 104°. If, however, the above mixture is heated at once at 100°, then a stereoisomeride is obtained melting at 153°. The compound melting at 104° separates in short, colourless crystals, immediately decolorises permanganate in alkaline solution, gives a white, voluminous precipitate with silver nitrate, and, when hydrolysed with alcoholic potash, yields an acid which sinters at 118°, and melts and decomposes at 155—160°. When treated with hydrogen bromide in cold acetic acid, it is converted into the isomeride melting at 153°; this crystallises in colourless needles, is partially hydrolysed by boiling with water, and immediately decolorises alkaline permanganate solution. It cannot be obtained by treating the isomeride melting at 104° with hydrochloric acid as, under these conditions, hydrolysis takes place, and the *acid* $C_4H_4N_2(COOMe)_3 \cdot COOH$ is obtained. This crystallises in colourless needles, melts at 167°, and gives an acid reaction when dissolved in water.

Methylic trimethylene-1 : 2 : 3-*tricarboxy*-1-*acetate*,

$$COOMe \cdot CH {<} \begin{array}{l} C(COOMe) \cdot CH_2 \cdot COOMe \\ | \\ CH \cdot COOMe \end{array},$$
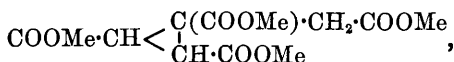
is obtained by heating the preceding compound at 160—190° under a pressure of 40 mm. mercury as long as nitrogen is evolved. It distils as a colourless oil at 210—215° under 40 mm. pressure. It crystallises in flat prisms and melts at 67°. When boiled with sodium hydroxide solution, it is converted into an "oxyglutaracetic acid," $C_4H_5(COOH)_3$, which, owing to its extreme solubility, cannot be isolated. When heated with sodium carbonate solution at 60° it yields the lactonic acid, $C_5H_6O_2(COOH)_2$. This crystallises in small, colourless nodules, melts at 190°, is not acted on by alkaline permanganate, and is converted into the preceding oxy-acid when treated with normal solution of sodium hydroxide. E. C. R.

Action of Ethereal Diazoacetates on Ethereal Salts of Unsaturated Acids.

By E. BUCHNER and H. DESSAUER (*Ber.*, **27**, 877—879; 879—881).—*Methylic methylpyrazoline*-3 : 4 : 5-*tricarboxylate*, $NH{<}\begin{array}{l} CH(COOMe) \cdot CMe \cdot COOMe \\ | \\ N{=\!=\!=\!=}C \cdot COOMe \end{array}$, is obtained by heating methylic citraconate with methylic diazoacetate at 60°, and gradually raising the temperature to 120°; it crystallises in tufts of long prisms, and melts at 86°. The authors were unable to isolate a stereoisomeride, although, according to theory, this should exist.

Methylic methyltrimethylenetricarboxylate is obtained by decomposing the preceding compound by heat. It distils as a colourless oil at 170—180°, under 30 mm. pressure, crystallises in flat, colourless needles, melts at 77°, and is stable towards alkaline permanganate. The *free acid*, $COOH \cdot CMe {<} \begin{array}{l} CH \cdot COOH \\ | \\ CH \cdot COOH \end{array}$, is obtained by the hydrolysis of the methylic salt. It crystallises in colourless nodules, melts at 191°, without decomposition, and is not acted on by alkaline permanganate.

It is apparently unaltered by boiling with permanganate or with dilute nitric acid.

Methylic pyrazolinedicarboxyacetate,

$$N\!\!<\!\!^{NH \;\overline{\quad\quad\quad\quad}}_{C(COOMe)\cdot CH_2}\!\!>\!\!C(COOMe)\cdot CH_2\cdot COOMe,$$
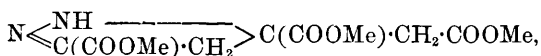
is obtained by mixing methylic itaconate and methylic diazoacetate at the ordinary temperature. It crystallises in colourless, interlacing needles, melts at 91°, and is not altered by heating with hydrogen bromide in acetic acid solution. When heated under diminished pressure at 160—180°, it yields a bright yellow oil, which distils at 190—200°, contains no nitrogen, and remains uncrystallised after the lapse of years. This compound quickly decolorises alkaline permanganate, and, when hydrolysed with aqueous sodium hydroxide, yields a mixture of a saturated and an unsaturated acid. The latter, owing to its great solubility, could not be isolated. The saturated acid was identified as a *trimethylene-*1 : 2-*dicarboxy-*1-*acetic acid.* It crystallises in colourless crusts, begins to decompose at 180°, melts at 212° with decomposition, does not decolorise alkaline permanganate, and is not altered by boiling with a normal solution of sodium hydroxide.

E. C. R.

Transformation of Ketazines into Pyrazolines. By T. Curtius and H. A. Försterling (*Ber.,* **27,** 770—773).—1f dimethylketazine, $CMe_2\!:\!N\cdot N\!:\!CMe_2$, obtained by the action of hydrazine hydrate on acetone, is treated with maleïc acid, or if acetone is treated with hydrazine maleate, *trimethylpyrazoline maleate* is formed. This crystallises in colourless needles, melts at 127°, and is decomposed by dilute acids and alkalis into its constituents; with concentrated caustic soda, however, it yields, not maleïc, but fumaric acid. The *trimethylpyrazoline,* $^{N=CMe}_{NH\cdot CMe_2}\!\!>\!\!CH_2$, obtained from it is identical with that obtained from hydrazine hydrate and mesityl oxide; its *hydrochloride* melts at 170°, its *picrate* at 138°.

Fumaric acid effects the same transformation, but not spontaneously, prolonged heating at 100° being necessary.

Hydrazine maleate, $C_2H_2(COOH)_2,N_2H_4 + 2H_2O$, forms colourless needles.

C. F. B.

5-Phenylpyrazoline. By R. v. Rothenburg (*Ber.,* **27,** 788—790).—Cinnamylideneazine, $N_2(CH\cdot CH\!:\!CHPh)_2$, prepared from hydrazine and cinnamaldehyde (Curtius and Jay, Abstr., 1899, 393), when heated at 120° with excess of hydrazine hydrate, yields 5-*phenylpyrazoline,* $^{N=CH}_{NH\cdot CHPh}\!\!>\!\!CH_2$, an oil which, when oxidised, does not yield Buchner's 5-phenylpyrazole (Abstr., 1893, i, 282). Buchner's compound is, therefore, probably 3-phenylpyrazole. Hydrochloric acid converts it into a dimolecular polymeride, the platinochloride of which has the formula $2(C_9H_{10}N_2)_2,H_2PtCl_6 + 7H_2O$.

With hydrazine hydrate, benzoylaldehyde yields what is probably a mixture of 3- and 5-phenylpyrazole. Sodio-acetoacetaldehyde

and hydrazine acetate yield methylpyrazole, the platinochloride of which, $2C_4H_6N_2,H_2PtCl_6$, was prepared.

Hydrazine hydrate can be prepared, without using a silver retort, by precipitating a boiling solution of hydrazine sulphate with a boiling solution of barium hydroxide, and fractionating the filtered solution. The yield is 70—80 per cent. of the theoretical, and the rest of the hydrazine can be recovered as sulphate from the impure fractions. C. F. B.

Pyrazolone Reactions. By R. v. ROTHENBURG (*Ber.*, **27**, 782). —An enumeration of the reactions of derivatives of pyrazolone, $\genfrac{}{}{0pt}{}{N\!=\!CH}{NH\cdot CO}\!\!>\!CH_2$. It can only be said, by way of extract, that pyrazolones can be readily oxidised, but do not undergo any simple hydrolysis. Substituting and other agents chiefly attack the CH_2-group, both the hydrogens of which can be replaced by bromine, by the group $:CHR$ from aldehydes, or by $:NOH$ from hydroxylamine, whilst one of them can be replaced by the group $\cdot N:NR$ of diazocompounds, azo-derivatives being formed. If both these hydrogens are replaced, the product is insoluble in alkalis; if only one, it is soluble, the remaining H doubtless moving to the adjacent C of the CO-group to form the tautomeric pyrazolidone. Nitrous acid forms nitroso-derivatives of pyrazolones, but here the NH-group is doubtless attacked. C. F. B.

Pyrazolones from Phenylpropiolic acid, and their Azo-derivatives. By R. v. ROTHENBURG (*Ber.*, **27**, 783—787).—Phenylpropiolic acid condenses with hydrazine hydrate to form 3-*phenyl-pyrazolone*, $\genfrac{}{}{0pt}{}{N:CPh}{NH\cdot CO}\!\!>\!CH_2$, melting at 236°. The *benzal* and *isonitrosoderivatives* (compare preceding abstract) melt above 250° and at 184° respectively; the *silver salt* of the latter decomposes at 242°. The *phenyl-, ortho-* and *para-tolyl-,* and α- and β-*naphthyl-* azo-derivatives melt at 208°, 179°, 185°, 216°, and above 250° respectively; when reduced, all of them yield, the same *rubazonic acid*, $C_{18}H_{13}N_5O_2$, melting at 124°. With phenylhydrazine, phenylpropiolic acid condenses to form Knorr and Klotz's 1 : 3-*diphenylpyrazolone* (Abstr., 1887, 1121). The *benzal-* and *isonitroso-,* and the *azo-derivatives* as before, melt at 146°, 199°, 170°, 226°, 242°, 196°, and 225° respectively; on reduction, the azo-derivatives all yield the *rubazonic acid*, $C_{30}H_{21}N_7O_5$ (melting at about 200° ?).

3-*Carboxypyrazolone-4-orthoazobenzoic acid*,

$$\genfrac{}{}{0pt}{}{N:C(COOH)}{NH\!-\!\!-\!\!-\!CO}\!\!>\!C:N\cdot NH\cdot C_6H_4\cdot COOH,$$
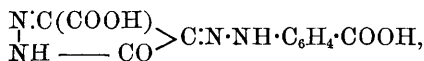
and its *ethylic salt*, melting respectively at 227° and 255°, are obtained from pyrazolone-3-carboxylic acid and its ethylic salt by means of orthodiazobenzoic acid.

The latter part of the paper is devoted to a few remarks on the constitution of pyrazolones, and their relation to isopyrazolones. C. F. B.

Pyrazolones from Dehydracetic and Coumalinic acids. By R. v. ROTHENBURG (*Ber.*, **27**, 790—792).—Dehydracetic acid yields 3-methylpyrazolone when heated at 120° with hydrazine hydrate and a little alcohol. It thus behaves just like ethylic acetoacetate, and this, the author thinks, favours Feist's view as to its constitution.

Dehydrobenzoylacetic acid yields 3-phenylpyrazolone in a similar manner.

Coumalinic acid, under rather different circumstances, yields pyrazolone itself, but it is necessary to work very cautiously, carefully avoiding any violent action. C. F. B.

Isomeric *n*-Phenylpyrazolones. By R. v. ROTHENBURG (*Ber.*, **27**, 946—948).—The author maintains, in opposition to Stolz (this vol., i, 259), that the isomeride melting at 118° is 1-phenyl-3-pyrazolone, whilst that melting at 153° has the constitution of a 1-phenyl-5-pyrazolone. A. H.

Nomenclature of the Pyrazolones. By R. v. ROTHENBURG (*Ber.*, **27**, 957—958).—Knorr's suggestions, made in 1887 (*Annalen*, **238**, 137—219), on this subject are criticised, and the terms *pyrazolone* and *isopyrazolone* are employed to distinguish the groups

$$CO<^{\overset{1}{NH}\cdot\overset{2}{N}}_{\underset{4}{CH_2}\cdot\underset{3}{CH}} \quad \text{and} \quad CO<^{\overset{1}{NH}\cdot\overset{2}{NH}}_{\underset{4}{CH}:\underset{3}{CH}},$$
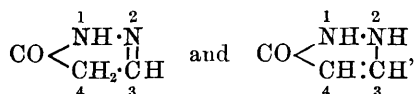
instead of 5-pyrazolone and 3-pyrazolone respectively, the positions of substituting elements being indicated by numbers. Knorr's 1-phenyl-3-methyl-5-pyrazolone and 1-phenyl-2 : 3-dimethyl-3-pyrazolone (antipyrine) would therefore be called 1-phenyl-3-methylpyrazolone and 1-phenyl-2 : 3-dimethylisopyrazolone. J. B. T.

New Synthesis of Diketoquinazolines. By A. STEWART (*J. pr. Chem.*, [2], **49**, 318).—From the interaction of anthranilic acid, and orthamidobenzamide, respectively, with phenylic isocyanate, compounds are obtained which yield diketo-γ-phenylquinazoline (m. p. 273—274°) when treated with dehydrating agents. The interaction of carbamide with alkylamides directly yields diketo-γ-alkylquinazolines (compare Abstr., 1889, 609); in this way diketo-γ-ethylquinazoline (m. p. 195—196°; Söderbaum, Abstr., 1890, 1254) and diketo-γ-allylquinazoline (m. p. 183°) were obtained. A. G. B.

Formation of Diketoquinazolines from Substituted Anthranilic acids. By W. WIELANDT (*J. pr. Chem.*, [2], **49**, 319—320; compare preceding abstract).—By melting benzylanthranilic acid (m. p. 169—170°) with carbamide (equivalent proportions), *carbamidobenzylanthranilic acid*, $COOH\cdot C_6H_4\cdot N(C_7H_7)\cdot CONH_2$, is formed. With excess of carbamide, *benzyldiketoquinazoline*, $C_6H_4<^{CO\cdot NH}_{N(C_7H_7)}>CO$, is produced; it does not melt, but decomposes above 360°. *Phenyldiketoquinazoline*, $C_6H_4<^{CO\cdot NH}_{NPh\,—}>CO$, a microcrystalline powder

decomposing above 360°, is the only product of the interaction of phenylanthranilic acid and carbamide.

Trinitrophenylanthranilic acid (m. p. 265—266°) and urea yield *trinitrophenyldiketoquinazoline*, $\begin{matrix} NH-CO \\ | \\ CO \cdot C_6H_4 \end{matrix} > N \cdot C_6H_4(NO_2)_3$, which crystallises in pale yellow needles.

Benzylanthranilic acid and phenylic isocyanate yield the *compound* $COOH \cdot C_6H_4 \cdot N(C_7H_7) \cdot CO \cdot NHPh$ (m. p. 165—166°); phenylanthranilic acid and phenylic isocyanate yield *diphenyldiketoquinazoline* (m. p. 234—235°); trinitrophenylanthranilic acid and phenylic isocyanate yield *phenyltrinitrophenyldiketoquinazoline* (m. p. 237—238°); the two latter compounds are also produced by the interaction of the acids with phenylcarbamide.

By substituting thiocarbamide for carbamide, products free from sulphur are obtained. The investigation is proceeding.

A. G. B.

Cinchonifine. By E. JUNGFLEISCH and E. LÉGER (*Compt. rend.*, 118, 536—538).—Cinchonifine is best obtained by crystallising from large quantities of strong, boiling alcohol that portion of the cinchonine bases which is insoluble in ether or in dilute alcohol. The cinchonifine separates on cooling, whilst apocinchonine and cinchonibine remain in solution. The purification is accelerated by converting the cinchonifine into basic sulphate, which is crystallised repeatedly from hot water, the free base being subsequently crystallised from boiling alcohol.

Cinchonifine forms small, brilliant, colourless, anhydrous needles, insoluble in water, ether, or dilute alcohol, and very slightly soluble in alcohol or in chloroform, but soluble in a mixture of the two. It melts at 273·6° (corr.) and, when more strongly heated, decomposes and volatilises. It is dextrogyrate in alcoholic solution; at 17° $[\alpha]_D = + 201·4°$ with a solution of 0·75 gram in 100 c.c., but the rotatory power increases with the concentration. A 1 per cent. solution in dilute hydrochloric acid (2HCl) gives $[\alpha]_D = + 228·9°$, or with $4HCl + 226·3°$; a 1·5 per cent. solution with 2HCl gives $[\alpha]_D = + 225·13°$.

Cinchonifine is alkaline to litmus, but not to phenolphthalein; it yields two classes of salts which as a rule are very soluble in water and crystallise well. The basic hydrochloride forms silky needles which contain $2H_2O$ and melt at about 208°; the zincochloride forms anhydrous rhombic prisms; the aurochloride and platinochloride are yellow and imperfectly crystalline; the basic hydrobromide forms very soluble needles which contain $1H_2O$ and melt at about 221°; the basic hydriodide forms colourless, long, flattened prisms which contain $1H_2O$; the basic nitrate forms highly refractive, rhombic crystals, which contain $1H_2O$; the basic thiocyanate forms long, flattened anhydrous prisms; the basic sulphate forms efflorescent, prismatic needles, with $2H_2O$, but when anhydrous melt at about 188°; the basic oxalate forms long, slender needles, which contain $1H_2O$, and are much more soluble in hot water than in cold; the basic succinate is very soluble in water, but insoluble in solutions of alkali succinates, and crystallises in prismatic needles,

which contain $1H_2O$; the basic tartrate forms flattened elongated prisms which contain $1\frac{1}{2}H_2O$ and melt with decomposition at about 209°; the normal tartrate is less soluble than the basic salt, and crystallises in prismatic needles containing $4H_2O$.

Cinchonifine methochloride forms large, colourless needles with $2H_2O$; the methiodide forms short, anhydrous prisms, which melt with decomposition at 251°, but if crystallised at a low temperature it forms thin plates which contain $2H_2O$. The dimethiodide forms very soluble lemon-yellow plates, which contain $1\frac{1}{2}H_2O$ and melt and decompose at about 223°. The ethiodide forms long, slender, colourless, anhydrous needles, which melt and decompose at about 251°, and are insoluble in ether; the diiodoethide forms lemon-yellow anhydrous plates which melt with decomposition at about 225°. The ethobromide crystallises with $3H_2O$ in bulky prisms which melt and decompose at about 225°, and the diethobromide forms hard, anhydrous, crystalline crusts which melt at about 218°.   C. H. B.

Isomeride of Brucine Methiodide. By E. LIPPMANN (*Monatsh.,* **15**, 116—117; compare Abstr., 1893, i, 738).—On heating an alcoholic solution of brucine hydriodide with methylic iodide, in sealed tubes, at 100°, a colourless salt is obtained, which is converted by ammonia into an isomeride of brucine methiodide. It crystallises from water in slender prisms, which become transparent at 198—200°, and decompose rapidly at 260°. The previously described isomeride, on the other hand, blackens at 270° and decomposes at 280°. The formation of these two isomerides is easily understood, when it is remembered that the two nitrogen atoms in brucine are quite different in their functions, one occurring in a quinoline ring, the other in what is probably either an indole- or a carbazole-group.

G. T. M.

Reducing Substance from Serum-Globulin. By K. A. H. MÖRNER (*Chem. Centr.*, 1894, i, 333—334; from *Centr. Physiol.*, **7**, 581—583).—Serum-globulin, precipitated either by the acetic acid or magnesium sulphate method, and heated in the water-bath with 3—5 per cent. hydrochloric acid, yields a substance which reduces Fehling's solution. Serum-globulin coagulated by heat, also that from morbid urine and ascitic fluid, behaves similarly. Myosin, vitellin, crystallin, fibrinogen, serum-albumin, and egg-albumin do not. Fibrin obtained by whipping blood yields a reducing substance, due, probably, to entangled corpuscles. The reducing substance yields an osazone melting at 170—172°, is optically inactive, and only feebly reduces alkaline bismuth solutions.   W. D. H.

Organic Chemistry.

Nomenclature. By E. SEELIG (*J. pr. Chem.*, [2], **49**, 407—408). —The author has elsewhere suggested some changes in the nomenclature of organic compounds ; these he indicates in this paper.

A. G. B.

Odour of Alkylic Sulphides. By J. FINCKH (*Ber.*, **27**, 1239—1241).—Commercial amylic sulphide, when heated with powdered copper for 6—8 hours at 290—300°, and subsequently fractionated, had an agreeable, sweet, ethereal smell, but its boiling point and composition were unchanged ; the residual copper contained considerable quantities of sulphur, and had a garlic odour. On treating the purified sulphide with a fresh quantity of copper, the latter was practically unchanged. Ethylic sulphide, after being heated three times successively with fresh portions of copper, still retained a trace of its characteristic odour, and methylic sulphide behaved in the same way ; in both cases, small quantities of combustible gas were formed during the experiments, but the boiling point was scarcely affected and the composition remained unaltered. Attempts to deodorise the preceding sulphides by means of olive oil, paraffin, wax, &c., were unsuccessful. Ethyl mercaptan resembles ethylic sulphide in its behaviour towards copper, but a considerable quantity is decomposed during the process.

J. B. T.

Polyhydric Alcohols Synthesised from Aldehydes and Ketones by Means of Formaldehyde. By M. APEL and B. TOLLENS (*Ber.*, **27**, 1087—1090).—Tollens and others (Abstr., 1892, 127 ; 1893, 617) have shown that formaldehyde reacts with other aliphatic aldehydes, yielding polyhydric alcohols ; several $CH_2 \cdot OH$ groups derived from the formaldehyde replace hydrogen atoms in the hydrocarbon residue of the second aldehyde.

Pentaglycol, $CMe_2(CH_2 \cdot OH)_2$, is obtained on warming a mixture of isobutaldehyde, formaldehyde, calcium hydroxide, and water, removing the calcium by means of oxalic acid, and distilling the solution after evaporation. It melts at 129° and boils at about 110° in a vacuum. The *diacetyl* derivative is a liquid boiling at about 85° in a vacuum, whilst the *dibenzoyl* derivative forms crystals melting at 53°.

Mayer (*Annalen*, **265**, 340) found that a mixture of formaldehyde, acetone, calcium hydroxide, and water, yielded a viscid liquid after removal of the lime ; the authors have obtained this product in a crystalline state. It is the *anhydride*, $C_9H_{18}O_6$, of the heptahydric alcohol, $OH \cdot CH(C[CH_2 \cdot OH]_3)_2$, and is, consequently, itself a pentahydric alcohol ; it melts at 156°. The *pentacetyl* derivative, $C_9H_{13}O(OAc)_5$, melts at 84°, and the *tetrabenzoyl* derivative at 153—154°.

W. J. P.

Combination of Iodine with Starch. By E. G. ROUVIER (*Compt. rend.*, **118**, 743—744).—When an aqueous solution of starch is mixed with iodine in excess, but in quantity insufficient to form the com-

pound $(C_6H_{10}O_5)_{16}I_5$, the quantity of iodine absorbed increases with the quantity added (Abstr., i, 1893, 683). The proportion of iodine that enters into combination for a given quantity of iodine added decreases, however, as the percentage of iodine in the product increases. When this percentage is between 13 and 17·5, the quantity of iodine taken up is practically equal to the cube root of the quantity of iodine added. Below 13 per cent., the quantity of iodine taken up increases more rapidly, but, on the other hand, above 17·5 per cent. it increases much more slowly.

Rice starch behaves in exactly the same way as wheat starch, but potato starch seems to combine with a smaller proportion of iodine even in presence of a large excess of the latter. C. H. B.

Natural Oxycelluloses. By C. F. CROSS, E. J. BEVAN, and C. BEADLE (*Ber.*, **27**, 1061—1065 and 1456).—The authors have previously shown (this vol., i, 63) that the production of furfuraldehyde by distilling celluloses with a mixture of sulphuric and hydrochloric acids is not conditioned by the presence of a pentaglucose group in the molecule. They now characterise more fully a group of oxycelluloses containing more oxygen and less carbon than normal cotton-wool celluloses; these yield furfuraldehyde on heating with sulphuric and hydrochloric acids, but give none of the reactions of the pentoses or pentosans; they are, moreover, characterised by their relative stability in respect of alkaline hydrolysis.

The celluloses of the grasses were first examined; of these, the oat-straw and esparto celluloses were found to yield well-characterised oxycelluloses of the above type. These celluloses contain 41—42 per cent. of carbon and 5·4—5·8 per cent. of hydrogen, and on distillation with the mixed acids give 12—12·5 per cent. of furfuraldehyde. Such "celluloses" as these must be distinguished from the normal ones, and may be classified as oxycelluloses. They are further characterised by giving a yellow colour with salts of phenylhydrazine, which becomes more intense on heating; they also give a magenta colour with magenta decolorised by sulphurous acid, and reduce boiling Fehling's solution.

The authors are continuing the investigation; more especially in its bearings on plant physiology. W. J. P.

Oxidation of Unsaturated Brominated Hydrocarbons. By C. H. v. HOESSLE (*J. pr. Chem.*, [2], **49**, 403—406).—The oxidation of brominated unsaturated hydrocarbons by alkaline permanganate produces hydroxyketones or hydroxyaldehydes, as expressed by the general equation $R^1CBr{:}CHR^2 + O + H_2O = R^1CO{\cdot}CH(OH)R^2 + HBr$.

Vinylic bromide yields glycolaldehyde; β-bromopropylene yields acetol; bromopseudobutylene yields methylacetylcarbinol (dimethyl-ketol); bromobutylene yields α-hydroxybutyric aldehyde, and bromo-cinnamene yields the aldehyde $OH{\cdot}CHPh{\cdot}CHO$ by such oxidation. Bromostilbene and bromophenanthrene are not attacked. A. G. B.

Butylchloral. By M. TARUGI (*Gazzetta*, **24**, i, 229—236).—The author confirms Pinner's description (*Annalen*, **179**, 40), of α- and

β-butylchloralacetamide; they melt at 158° and 170° respectively. The α- and β-butylchloralbenzamides, however, melt at 135° and 146° respectively, instead of at 150° and 170° as stated by Pinner.

Two *butylchloralformamides*, $C_2HMeCl_3 \cdot CH(OH) \cdot NH \cdot COH$, are produced by the interaction of formamide and butylchloral; they may be separated by crystallisation from dilute alcohol. The α-compound melts at 125° and the β- at 132°.

On distilling α- and β-butylchloralacetamides with dilute sulphuric acid, they seem to yield the same butylchloral hydrate. The two hydrates are, however, certainly different, for on treating the one derived from the α-amide with acetamide the α-compound is regenerated, whereas the hydrate from the β-amide yields β-butylchloralacetamide (compare Schiff, Abstr., 1891, 1067). The difference does not seem to be due to optical isomerism. W. J. P.

Amidoketones of the Fatty Series. By S. GABRIEL and T. POSNER (*Ber.*, **27**, 1037—1045).—Amidopropyl methyl ketone, $COMe \cdot CHEt \cdot NH_2$ (Abstr., 1893, i, 734), is partially converted into dimethyldiethylpyrazine when its hydrochloride is treated with soda.

Benzenesulphamidopropyl methyl ketone, $SO_2Ph \cdot NH \cdot CHEt \cdot COMe$, obtained by the action of benzenesulphonic chloride on the hydrochloride of the base, forms a white crystalline powder melting at 121°. Potassium cyanate reacts with the hydrochloride of the base to form ethylmethylimidazolone, $CO{<}^{NH \cdot CMe}_{NH \cdot CEt}$, which crystallises from hot water in colourless plates melting and decomposing at 270°. Potassium thiocyanate reacts in a similar manner, forming *ethylmethylimidazolyl-μ-mercaptan*, $SH \cdot C{\ll}^{NH \cdot CMe}_{N—CEt}$, which crystallises in yellowish plates, is soluble in alkalis, and does not melt below 320°. Oxidation by means of alcoholic ethylic nitrite converts the base into *ethylmethylglyoxaline*, $HC{\ll}^{NH \cdot CMe}_{N—CEt}$, the *picrate* of which melts at 155—158°, and the *aurochloride* at about 167°. It is uncertain whether these compounds are $\alpha\beta$- or $\beta\alpha$-derivatives. Investigations are in progress to ascertain whether the base employed in these experiments is identical or isomeric with that obtained by the reduction of the isonitrosoketone described by Claisen and Manasse (Abstr., 1889, 584) as having the constitution $COPr \cdot CH:NOH$.

Derivatives of Amidoacetone.—The compound formed by the action of potassium thiocyanate on amidoacetone hydrochloride, is completely decomposed by nitric acid at 220°, and is also oxidised by bromine water, carbamide being formed. A mercaptole could not be prepared directly from amidoacetone, but *phthalimidoacetone ethylmercaptole*, $C_8H_4O_2:N \cdot CH_2 \cdot CMe(SEt)_2$, is formed when acetonylphthalimide is treated with ethylic mercaptan. It crystallises in colourless tablets melting at 71—72°, and is decomposed by hydrochloric acid with formation of phthalic acid, ethylic mercaptan, and amidoacetone.

Derivatives of Diamidoacetone.—Diamidoacetone, first obtained by Rügheimer (Abstr., 1889, 249), may also be obtained in small

2 c 2

amount, by the oxidation of hydroxytrimethylenediphthalimide (Abstr., 1888, 1294), by means of chromic acid. The *diphthalimido-acetone*, $CO(CH_2 \cdot N \colon C_8H_4O_2)_2$, thus formed, is only slightly soluble in the usual solvents, melts at 264—268°, and forms pointed crystals. The corresponding *amic acid*, $CO(CH_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot COOH)_2$, is a white, crystalline powder, melting at 105—107°. The amic acid is decomposed by strong hydrochloric acid, impure diamidoacetone being formed.

Derivatives of Diacetonamine.—Diacetonedithiocarbamic acid,

$$C_7H_{13}ONS_2,$$
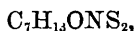
is prepared by the action of carbon bisulphide on diacetonamine in benzene solution. It forms colourless crystals, and melts at 119—120°. *Diacetonethiocarbimide*, $C_6H_{11}O \cdot NCS$, is prepared in the usual way from the foregoing compound. It is a colourless oil which decomposes when distilled. On treatment with an aqueous solution of hydrazine, it is converted into *diacetonethiosemicarbazide*,

$$C_6H_{11}O \cdot NH \cdot CS \cdot NH \cdot NH_2,$$

which is soluble in hot water, forms rhombohedral crystals, and melts at 148—151°. On treatment with sulphuric acid, it is converted into an *anhydro-compound*, $C_7H_{13}N_3S$, which forms a crystalline powder melting at 211—214°. A. H.

Preparation of Blue Copper Acetate. By C. ASTRE (*Chem. Centr.*, 1894, i, 141; from *J. Pharm.* [5], **28**, 542).—Wöhler states that these blue crystals are easily obtained by crystallising a solution of verdigris acidified with acetic acid. The author finds, however, that they are only formed when the density of the solution at 15° is 1·150 or above. In solutions of slightly lower density, a mixture of blue and green crystals is formed, and in those of less than 1·10, only green crystals. The blue crystals also form when moist verdigris is exposed to low temperatures. L. T. T.

β-Dimethylacrylic acid. By W. MASSOT (*Ber.*, **27**, 1225—1228). —When acetone is heated with malonic acid in the presence of acetic anhydride, dimethylacrylic acid, or isopropylideneacetic acid, $CMe_2 \colon CH \cdot COOH$, is formed, although the reaction does not occur when acetic acid is used instead of the anhydride (Komnenos, *Annalen*, **218**, 168). The acid crystallises from hot water in long, white needles melting at 69°. It combines with 1 mol. of bromine to form *αβ-dibromisovaleric acid* which is decomposed by the action of aqueous alkalis, α-bromisobutylene being formed. This substance is accompanied by a certain amount of *α-bromo-β-dimethylacrylic acid*, $CMe_2 \colon CBr \cdot COOH$, which crystallises in colourless needles melting at 87·5—88·5°.

It has been found very difficult to prepare the corresponding chlorine derivatives of dimethylacrylic acid in a state of purity. *Monochlorodimethylacrylic* acid melts at 80—81°. A. H.

Ethylic Sodacetoacetate. By DE FORCRAND (*Compt. rend.*, **118**, 922—925).—With the object of throwing further light on the con-

stitution of ethylic sodacetoacetate by determining its thermochemical constants, the author has first prepared the sodium derivative, starting from the pure ethereal salt boiling at 179·5—180·5° under 760 mm.; sp. gr. = 1·027 at 15°. The direct action of the metal on excess of the salt results in the formation of compounds containing excess of the ethereal salt, which cannot be expelled by heat, because the sodium derivative decomposes below 100°. Elion's process of acting on a solution of the ethereal salt in ether with dry sodium hydroxide suspended in ether, and Gevekoht's method of dissolving the calculated quantity of sodium in an ethereal solution of the salt, give products containing too high a proportion of sodium. Harrow's method of dissolving sodium in ethyl alcohol, adding ether, mixing with the calculated quantity of ethylic acetoacetate dissolved in ether, and then adding water (*Annalen*, **201**, 141), yields a pure hydrated salt, which, when dried on porous tiles, contains 13·33 per cent. of sodium, whilst the salt $C_6H_9NaO_3,H_2O$ would contain 13·53 per cent. More water is necessary to cause precipitation of the salt than is indicated by Harrow. When placed in a vacuum over phosphoric anhydride, the salt gradually loses water, without forming any definite hydrates intermediate between the monohydrate and the anhydrous salt.

The following results were obtained for the heat of dissolution at + 12°.

$$C_6H_9NaO_3,H_2O \ldots\ldots +0·20 \text{ Cal.}$$
$$C_6H_9NaO_3,1\tfrac{1}{8}H_2O \ldots +1·76 \text{ ,,}$$
$$C_6H_9NaO_3,\tfrac{1}{2}H_2O \ldots +2·38 \text{ ,,}$$

Comparison of these numbers shows that the heat developed is practically proportional to the fraction of a molecule of water added or lost. It would follow that

$C_6H_9NaO_3$ solid + H_2O liquid = $C_6H_9NaO_3,H_2O$
solid .... develops +4·19 Cal.
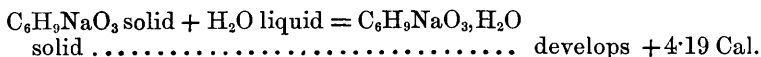
The partially dehydrated salt when dissolved in water and heated with dilute sulphuric acid gives the same development of heat as the hydrated salt, and hence the loss of water involves no change of constitution.

The author adopts +4·19 Cal. as the heat of hydration of anhydrous ethylic sodacetoacetate, and +4·39 for its heat of dissolution in 4 litres of water at +12°. C. H. B.

Reduction of Ethylic Isonitrosoacetoacetate. By S. GABRIEL and T. POSNER (*Ber.*, **27**, 1141—1144).—Ethylic isonitrosoaceto-acetate is reduced by tin and hydrochloric acid to *ethylic α-amidoaceto-acetate*, $CMeO·CH(NH_2)·COOEt$, the *hydrochloride* of which melts at 95° (it was mixed with a little ammonium chloride), the *picrate* at 129°. This substance in alkaline solution oxidises in the presence of air, to Wleügel's ethyl ketinedicarboxylate (dimethylpyrazinedicarb-oxylate), $C_4N_2Me_2(COOEt)_2$ (Abstr., 1882, 949); if it is mixed with aqueous potash and some copper sulphate, and distilled with steam, dimethylpyrazine is formed. When the hydrochloride is heated at 60° with phenylhydrazine, acetic acid, and aqueous sodium acetate,

Knorr's phenylmethylpyrazoloneazobenzene, $\begin{matrix} N{=}CMe \\ NPh{\cdot}CO \end{matrix}{>}C{:}N{\cdot}NHPh$ (Abstr., 1887, 602), is formed. When heated with potassium thiocyanate on the water-bath, it yields *ethylic mercaptomethylimidazolecarboxylate*, $\begin{matrix} CMe{\cdot}N \\ COOEt{\cdot}C{-}NH \end{matrix}{>}C{\cdot}SH$, melting, with decomposition, at 229°. Heated with potassium cyanate, it yields *ethylic methylimidazolonecarboxylate*, $\begin{matrix} CMe{\cdot}NH \\ COOEt{\cdot}C{-}NH \end{matrix}{>}CO$, melting at 220—221°.

<div align="right">C. F. B.</div>

Action of Hydroxylamine and Ethoxylamine on Ethylic Oxalate. By W. LOSSEN (*Ber.*, 27, 1105—1114).—When, to a solution of hydroxylamine hydrochloride (2 mols.) in the equivalent amount of baryta water, ethylic oxalate (1 mol.) is added, and caused to dissolve by shaking, a salt of an isomeric, bibasic, oxalhydroxamic acid, $C_2H_4N_2O_4$, is formed. The *barium, hydrogen, silver, calcium* (4H_2O), and *copper* (H_2O) salts of this acid were prepared; they all explode violently when heated to 50°, and mineral acids decompose them entirely, with formation of oxalic acid.

When ethylic oxalate (1 mol.) is gradually added to a methyl alcoholic solution of free hydroxylamine (3 mols.), the hydroxylamine salt of the ordinary oxalhydroxamic acid separates. This is the best method of preparing the acid.

When, to a solution of hydroxylamine hydrochloride (2 mols.) in the equivalent amount of alcoholic potash, ethylic oxalate (1 mol.) is added (after filtering from the precipitated potassium chloride), monobasic *hydroxyloxamic acid*, $COOH{\cdot}CO{\cdot}NH{\cdot}OH$ (perhaps, rather, *oxalmonhydroxamic acid*, $COOH{\cdot}C(NOH){\cdot}OH$), is formed. The *sodium* and *potassium salts* were prepared; they are very explosive. The *ethylic salt* was obtained, mixed with some of the acid, by mixing absolute alcoholic solutions of hydroxylamine and ethylic oxalate; by mixing methyl alcoholic solutions of hydroxylamine and methylic oxalate, the *methylic salt*, melting at 120°, was obtained. When the ethylic salt is decomposed with alcoholic potash, the *derivative*, $C_2HNO_4K_2 + \frac{1}{2}H_2O$, is formed, from which a corresponding *lead derivative* was prepared; the acid here functions as bibasic. Further, the methylic salt behaves like a monobasic acid; the methyl group is not displaced by the action of potash or ammonia, but the derivatives $C_2HMeNO_4Na + C_2H_2MeNO_4$ and $C_3H_4NO_4(NH_4)$ are formed. The latter is, doubtless, identical with Hantzsch's ammonium oxaminehydroxamate (this vol., i, 274). Hydroxylamine converts the methylic salt into a hydroxylamine salt.

When ethoxylamine (2 mols.) is mixed with ethylic oxalate (1 mol.) *ethylic oxalhydroxamate*, $C_2H_2N_2O_4Et_2$, melting at 153°, is formed. This functions as a bibasic acid; the very hygroscopic *potassium derivative*, and the *sodium, zinc, copper,* and *silver derivatives* were prepared; the *dimethylic derivative* was obtained as a colourless oil.

Ethylic iodide yields with silver oxalhydroxamate the compound

$C_2N_2O_4Et_4$; methylic iodide the corresponding compound, $C_2N_2O_4Me_4$; both are transparent oils. C. F. B.

Elimination of Carbonic Anhydride from Alkyl Substituted Malonic acids. By E. HJELT (*Ber.*, 27, 1177—1178).—The author has previously shown the influence of substituting groups on the relative speed of formation of anhydrides and lactones in this series of acids (Abstr., 1893, i, 693). The following determinations were made by heating 0·5 gram of each acid for 20 minutes at 145°, and titrating the residue with baryta water; the percentages of acid decomposed were as follows:—Malonic acid, 42·9; methylmalonic acid, 39·2; ethylmalonic acid, 42·5; propylmalonic acid, 44·9; iso-propylmalonic acid, 37·4; allylmalonic acid, 63·4; benzylmalonic acid, 69·8. The behaviour of the last two acids is due to the negative nature of the radicles; the influence of the isopropyl group is remarkable, as its presence greatly accelerates the formation of anhydrides. This reaction is conditioned chiefly by the chemical nature of the substituting radicles, and the influence which they consequently exercise on the stability of the atomic linkage; their weight and size appear to be of secondary importance. J. B. T.

Bromo- and Hydroxy-derivatives of Sebacic acid. By M. WEGER (*Ber.*, 27, 1210—1218).—When sebacic acid is treated with bromine and phosphorus tribromide, it is converted into a mixture of bromo-derivatives, from which white crystals melting at about 117°, and corresponding in composition with dibromosebacic acid, can readily be isolated by fractional precipitation from solution in aqueous sodium hydrogen carbonate, or by extraction of the crude mass with cold benzene. This acid has already been obtained (Claus and Steinkauler, Abstr., 1888, 133; Auwers and Bernhardi, Abstr., 1891, 1191), and is described as melting at about the temperature mentioned above. When, however, the crude mass is fractionally precipitated from ethereal solution by light petroleum, and the highest melting portions, thus isolated, further purified by conversion into the calcium salt, an acid is finally obtained, which melts sharply at 136°, and is the pure dibromosebacic acid. It is extremely soluble in alcohol, &c., slightly soluble in cold benzene, almost insoluble in light petroleum.

It was found impossible to isolate any definite substance containing less bromine from the oily portions of the brominated product.

Tetrabromosebacic acid, $C_{10}H_{14}Br_4O_4$, is formed when sebacic acid is heated with a large excess of bromine. It crystallises in plates, melts and decomposes at 165°, and is very readily soluble in ether, readily in benzene, and almost insoluble in light petroleum. The *sodium* salt, $C_{10}H_{12}Br_4O_4Na_2 + 9H_2O$, effloresces in the air.

When a solution of the normal sodium salt of the pure acid is boiled, dihydroxysebacic acid is produced. It forms efflorescent crusts, melts at 124°, and is readily soluble in cold water. On oxidation, it is converted into adipic and oxalic acids.

Monhydroxysebacic acid may be prepared from the sodium salt of the oily portion of the product of bromination of sebacic acid. It is

almost insoluble in cold water, and melts at 116°. On oxidation, it is converted into suberic and oxalic acids.

The acids described by Claus and Steinkauler (*loc. cit.*) were prepared from the impure bromo-product, and were themselves probably impure.   A. H.

Constitution of Ethylic Diacetosuccinate. By L. KNORR and F. HABER (*Ber.*, **27**, 1151—1167).—The isomeric relationships of the α-substituted ethylic acetacetates, of which ethylic diacetosuccinate is one, are first considered with the consequences resulting from their being (1) ketonic acids, (2) unsaturated alcoholic acids, (3) both ketonic and alcoholic acids in terms of Laar's hypothesis. In the first case, ethylic diacetosuccinate would exhibit the same isomeric forms as the tartarates. In the second case, it must exist in three stereo-isomeric forms,

$$
\begin{array}{ccc}
\mathrm{HO\cdot C\cdot Me} & \mathrm{Me\cdot C\cdot OH} & \mathrm{Me\cdot C\cdot OH} \\
\mathrm{COOH\cdot C\cdot C\cdot COOH} & \mathrm{COOH\cdot C\cdot C\cdot COOH} & \mathrm{COOH\cdot C\cdot C\cdot COOH} \\
\mathrm{Me\cdot C\cdot OH} & \mathrm{Me\cdot C\cdot OH} & \mathrm{HO\cdot C\cdot Me} \\
\mathrm{I.} & \mathrm{II.} & \mathrm{III.}
\end{array}
$$
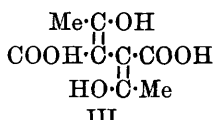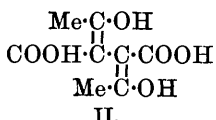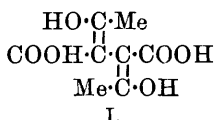
I would not yield either a γ-lactone or a furfuraldehyde derivative;

II would yield a lactone of the formula $\mathrm{COOH\cdot C\cdot C\cdot CO}$; III would
$$\begin{array}{c}\mathrm{MeC-O}\\ \mathrm{MeC\cdot OH}\end{array}$$

yield a dilactone, $\mathrm{CO\cdot C\cdot C\cdot CO}$, and also dimethylfurfurandicarboxylic
$$\begin{array}{c}\mathrm{MeC-O}\\ \mathrm{O-CMe}\end{array}$$

acid, $\begin{array}{c}\mathrm{MeC-O}\\ \mathrm{COOH\cdot C\cdot C(COOH)\!:\!CMe}\end{array}$. If ethylic diacetosuccinate is a tautomeric compound, six forms would be possible, and these are fully discussed and illustrated in the original paper.

Details of the preparation of ethylic diacetosuccinate by the action of iodine on ethylic sodacetoacetate are given; the yield is 40 per cent. of the theoretical. No isomeric compound is formed, and attempts to resolve it into active components by the action of *Penicillium glaucum, Potritis cynerea,* and *Saccharomyces ellipsoideus,* were unsuccessful. On heating the ethylic salt, alcohol is eliminated, and *ethylic isocarbopyrotritartrate (ethylic diacetosuccinate γ-lactone)* is formed, together with varying quantities of ethylic and diethylic dimethylfurfurandicarboxylates. Ethylic isocarbotritartrate is also formed by the action of alcoholic potash on ethylic diacetosuccinate, and the latter compound is regenerated from the former by heating with alcohol at 180°. It melts at 110°, and cryoscopic molecular weight determinations agree with the formula $C_{10}H_{12}O_5$. The *dibromo-derivative,* $C_{10}H_{10}Br_2O_5$, is insoluble in water, and crystallises in lustrous plates melting at 122°. The *nitro*-derivative, $C_{10}H_{11}O_5\cdot NO_2$, is crystalline, melts at 58—59°, and dissolves in alkalis with a yellowish-red colour. The corresponding compound of ethylic diacetosuccinate, $C_9H_{11}O_3\cdot NO_2$, crystallises from alcohol in colourless plates, melts at

55°, is insoluble in alkalis, and does not give Liebermann's reaction. By the action of ammonium acetate on ethylic isocarbopyrotritartrate, a compound $C_{10}H_{13}NO_4$, is formed, which crystallises from alcohol, melts at 220—221°, and does not show the pyrroline reaction. With aqueous ammonia, the ethereal salt yields a substance which crystallises from water, melts at 260°, and evolves ammonia on heating with soda. Unsymmetrical diphenylhydrazine yields a compound which crystallises in needles, melts at 187°, is not acted on by alkalis and hydrochloric acid, but dissolves in concentrated sulphuric acid; on adding nitric acid, a blue coloration is produced, changing to green and dull yellow.

By the action of alkalis on the lactone, crystalline salts of diacetosuccinic acid are formed; the *free acid* is unstable, and could not be isolated, like the alkali salts, it is converted into acetylacetone on boiling in aqueous solution. This hypothetical acid differs considerably from the diacetosuccinic acid previously prepared by the hydrolysis of ethylic diacetosuccinate with concentrated soda (*Ber.*, **20**, 171), the latter is therefore termed the α-form, and the unstable one the β-modification. Attempts to prepare a dilactone from the lactone were unsuccessful; on heating with concentrated sulphuric acid, it is converted into carbopyrotritartaric acid. The *strychnine salt* of the lactone crystallises in needles, and melts at 227—228°; failure to obtain an active acid from it renders the ketone formula for the lactone unlikely. The lactone and its ethereal salt spontaneously decompose, more or less rapidly, with formation of acetic acid.

These results indicate that β-diacetosuccinic acid has the formula II (see above), as this explains the ease with which it forms a monolactone, and the non-production of a dilactone. α-Diacetosuccinic acid is therefore either structurally isomeric with the β-acid, $COOH \cdot CHAc \cdot CHAc \cdot COOH$, or it has the formula I; in the former case, their relationship would be similar to that of the two forms of tribenzoylmethane, dibenzoylacetone, and ethylic formylphenylacetate. The formation of carbopyrotritartaric acid from α-diacetosuccinic acid and from isocarbopyrotritartaric acid is preceded by the conversion of both α- and β-diacetosuccinic acids into the γ-configuration, formula III (see p. 360). J. B. T.

Hydroxyterpenylic acid. By O. BEST (*Ber.*, **27**, 1218—1225). —When carvole is treated with aqueous potassium permanganate, it is converted into acetic acid, a non-volatile syrupy acid, which has not yet been examined, and *hydroxyterpenylic acid*,

$$C_8H_{12}O_5 = \begin{matrix} O-CMe_2 \\ | \\ CO \cdot CH_2 \end{matrix} > CH \cdot CH(OH) \cdot COOH.$$
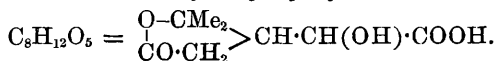
The latter crystallises from hot water in colourless needles, and melts at 190—192°. The salts are, as a rule, very soluble, and of a gummy character. The acid contains a lactone group, and combines with one molecule of potash in the cold, two on heating. It was found impossible to obtain the free bibasic acid, *hydroxydiaterpenylic acid*, $COOH \cdot CH_2 \cdot CH(CMe_2 \cdot OH) \cdot CH(OH) \cdot COOH$, by decomposing the salts formed by dissolving hydroxyterpenylic acid in alkalis, but its

silver salt, $C_8H_{12}Ag_2O_6$, was obtained in the form of a white precipitate. Hydroxyterpenylic acid is easily reduced by hydriodic acid to terpenylic acid, melting at 55—56°. *Methylic hydroxyterpenylate*, $C_9H_{14}O_5$. cannot be prepared by the etherification of the acid, but may be obtained by the action of methylic iodide on the silver salt; it is a thick, colourless oil. This same methylic salt is also formed when the silver salt of the bibasic hydroxydiaterpenylic acid is treated in the cold with methylic iodide.

When hydroxyterpenylic acid is distilled at a pressure of 10 mm. or treated with alcohol and hydrochloric acid, it yields a *dilactone*,

$$CO{<}^{CH_2\cdot CH\cdot CMe_2}_{O\,-CH-CO}{>}O,$$

melting at 129°; this substance requires one molecule of potash for neutralisation in the cold, but two on heating. When the solution in one molecule of potash is acidified, however, the dilactone itself is reproduced and not hydroxyterpenylic acid. With two molecules of potash, the salts of hydroxydiaterpenylic acid are formed. These results are best explained (compare Schryver, *Trans.*, 1893, 1327) by ascribing the formulæ given above to these derivatives.   A. H.

Citric acid and its Alkali Salts. By T. SALZER (*Arch. Pharm.*, **231**, 514—521; compare Abstr., 1892, 149).—Finely powdered citric acid becomes anhydrous when slowly heated at 55°, and in this condition melts at 160°. Buchner and Witter (Abstr., 1892, 824) have shown that anhydrous citric acid may be regenerated from its lead salt by decomposing it with hydrogen sulphide, whilst the corresponding lead salt obtained from the hydrated acid gives rise to the modification from which it is derived. On examining the sodium and potassium salts derived from the anhydrous acid, however, the author finds that they are identical with those of the hydrated form.

Monosodium citrate prepared from the anhydrous acid crystallises with $1H_2O$, and dissolves in about $4\frac{1}{2}$ parts of water at 18° and $1\frac{1}{4}$ parts at 100°, being slightly more soluble than the anhydrous salt. The disodium citrate described by Heldt is monhydrated, but the author's investigation points to the existence of a salt crystallising with $2\frac{1}{2}H_2O$, and soluble in about 3 parts of cold water; the greater part of the water of crystallisation is driven off at 100°.

Anhydrous monopotassium citrate (Abstr., 1892, 149) can be obtained in measurable crystals belonging to the triclinic system.
                                        M. O. F.

Stereoisomeric Butanetetracarboxylic acids. By K. AUWERS and A. JACOB (*Ber.*, **27**, 1114—1132; compare Abstr., 1893, i, 253). —If ethylic sodiomalonate is allowed to react with ethylic aconitate in benzene solution, and if not more than 1 atom of sodium is present for each molecule of the malonate, then no ketopentamethylenedicarboxylate is formed, as when alcohol is employed as a solvent, but a mixture is obtained from which only the two acids melting at 185° and 244° (more correctly 189° and 232°) can be isolated. These are shown to be stereochemically isomeric butanetetracarboxylic acids, and are distinguished by the letters *h* and *n* prefixed respectively to the acid of higher and of lower (*niedriger*) melting point. Each acid

yields ethereal salts and anhydrides, and the members of the two series are interconvertible, as appears below.

The starting point is *n-butanetetracarboxylic acid*,

COOH·CH₂·CH(COOH)·CH(COOH)CH₂(COOH),
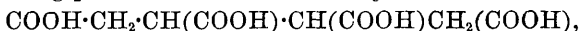
melting at 189°. The product of the above-mentioned action is heated with hydrochloric acid, the crystals of the two acids collected, dried, and boiled with acetic anhydride, when, from both acids, the anhydride of the *n*-acid is formed. From the latter, by dissolving it in water and crystallising, the *n*-acid can itself be obtained. The *tetramethylic, diethylic*, and *dipropylic salts* melt at 75—76°, 168°, and 129°; the *tetrethylic salt*, which, unlike the others, was prepared by the aid of heat, is an oil boiling at about 300°. The acid itself, in acetic acid solution, has an abnormal molecular weight (=153) as determined cryoscopically; its sodium salt, like that of its isomeride, exhibits a much smaller dissociation in solution than is the case with other tetracarboxylic acids. When the acid is heated to boiling with a large excess of acetic anhydride, it is immediately converted into the *n-dianhydride*, C₈H₆O₆; this crystallises in small octahedra with adamantine lustre, softens at 245°, and melts at 248°, is attacked only very slowly by sodium carbonate in the cold, and gradually absorbs moisture, becoming reconverted into the acid. If the *n*-acid is heated at 190° with nitrobenzene, it yields the *h-mono-anhydride*, C₈H₈O₇; this forms small, nacreous plates, softens at 228°, and melts and decomposes at 232°. Cold water hardly dissolves it, but boiling water converts it into *h-butanetetracarboxylic acid*, which melts at 236°, and is less soluble in water than the *n*-acid; the *tetramethylic salt* of this acid melts at 63—64°. When this acid is heated for two days with acetic chloride at 100° in a sealed tube, it yields the *h-dianhydride*, which melts at 168° (not at 172—173°, as previously given), and is readily attacked by sodium carbonate. It can be converted into the *n*-isomeride by boiling it for a few minutes with nitrobenzene. C. F. B.

Urethane. By A. HANTZSCH (*Ber.*, **27**, 1248—1254).—*Dichlorethylenurethane*, CCl₂:C:N·COOEt, is prepared by the action of sodium ethoxide on anhydrochloralurethane, CCl₃·CH:N·COOEt (Abstr., 1891, 1003), and crystallises from alcohol in stellate needles melting at 37°. It is readily volatile with steam, and has an odour of carnations. Urethane and glyoxalic acid yield a compound

COOH·CH(NH·COOEt)₂,

crystallising in colourless needles which melt at 156°. The condensation product of urethane and trichloracetic cyanide is oily; with paranitraniline the cyanide combines to form *trichloracetoparanitranilide*, CCl₃·CO·NH·C₆H₄·NO₂, which is crystalline, and melts at 142°. Urethane and benzaldehyde, in presence of sodium ethoxide, yield benzylidenediurethane.

Oxalyldiurethane, C₂O₂(NH·COOEt)₂, is prepared from ethylic oxalate and urethane in presence of sodium ethoxide; it is crystalline, and melts at 170°. Ethylic salts of the fatty acids do not combine with urethane.

Ethylic dibromamidocarboxylate sodium bromide, 4NBr$_2$·COOEt + NaBr, is formed by the action of bromine and soda on urethane, as a yellow, granular powder; the sodium bromide is not removed by washing with water; it melts and decomposes at 136°, and also decomposes slowly at ordinary temperatures in presence of moisture. The yield is almost quantitative. The *potassium salt* closely resembles the sodium compound; both react violently with ammonia or ammonium carbonate. By the action of ether, carbon bisulphide, or chloroform on the salts, *ethylic dibromamidocarboxylate* is obtained; this is a yellowish-red, unstable oil, has a penetrating odour, and reacts with anhydrous ammonia to form nitrogen and urethane. By the action of sodium amalgam on the preceding compound, or on the additive product, a complex reaction takes place resulting in the formation of *bromethylidenediurethane*, CH$_2$Br·CH(NH·COOEt)$_2$, which crystallises in colourless needles, melts at 142—143°, and closely resembles the corresponding chloro-derivative. On boiling with dilute hydrochloric acid, it is resolved into bromaldehyde and urethane. Ethylic dibromamidocarboxylate therefore reacts with ether like free bromine, converting it into bromaldehyde, which then, in presence of hydrogen bromide, condenses with the urethane. *Dibromethylidenediurethane*, CHBr$_2$·CH(NH·COOEt)$_2$, is formed by the decomposition of ethylic dibromamidocarboxylate in presence of moisture; it is crystalline, and, like the dichloro-compound, melts at 120°.

J. B. T.

Hydroxyurethane and certain reactions of Benzhydroxamic acid. By A. HANTZSCH (*Ber.*, **27**, 1254—1257).—Ethylic carbonate reacts less readily with hydroxylamine than the ethylic salts of fatty acids. *Hydroxyurethane*, OH·NH·COOEt or OH·C(OEt):NOH, is prepared by the interaction of hydroxylamine hydrochloride and ethylic carbonate in aqueous solution with soda, or, better, in alcoholic solution with sodium ethoxide; the yield is increased if ethylic chlorocarbonate is substituted for the ethylic carbonate. It is a colourless, odourless liquid, miscible in all proportions with water, yields a dark violet coloration with ferric chloride, and is more stable towards acids than the true hydroxamic acids; alkaline copper solution is only reduced by prolonged boiling and evaporation with hydrochloric acid. The *copper salt* is green and slimy.

The following experiments had for their object the conversion of hydroxamic acids, OH·CR:NOH, into anhydrides, RC$\overset{N}{\underset{O}{<}}$. Hydroxyurethane, if heated with phosphorous pentachloride, but not with phosphoric anhydride, yields a yellow oil which is not an anhydride but probably the chloro-derivative OEt·CCl:NOH. *Benzhydroxamic acid acetate*, OH·CPh:NOAc, is relatively stable, and crystallises from water; it melts 1° higher than the acid, and, on strongly heating, yields phenylic isocyanate. On gently warming with potash, it is hydrolysed yielding benzhydroxamic acid, but, with potassium carbonate, diphenylcarbamide and some aniline are formed; this reaction resembles that of benzaldoxime acetate, and is not given by benzhydroxamic acid; in all probability the anhydride CPh$\overset{N}{\underset{O}{<}}$ is first

formed, then, by intramolecular rearrangement, phenylic isocyanate, which reacts with the water to form diphenylcarbamide.

J. B. T.

Amidosulphonic acids. By C. PAAL and F. KRETSCHMER (*Ber.*, **27**, 1241—1247).—*Ethylic amidosulphonate*, $NH_2 \cdot SO_3Et$, is obtained from ethylic iodide and silver amidosulphonate as an oily liquid, which decomposes on distillation; it is completely miscible with water or alcohol, and by the action of water or of alcoholic ammonia is converted into ammonium ethylic sulphate. The silver salt, $NH_2 \cdot SO_3Ag$, has recently been prepared by Eitner, and crystallises in colourless, lustrous needles. The *copper salt* crystallises in small, blue, the *lead salt* in colourless, needles. The *aniline salt*, $NH_2 \cdot SO_3 \cdot NH_3Ph$, is prepared by mixing the constituents in warm aqueous solution, and is deposited in large, colourless plates; it melts at 148—149°, and is slowly decomposed by prolonged heating in aqueous or alcoholic solution.

Ammonium anilidosulphonate, $NHPh \cdot SO_3 \cdot NH_4$, is prepared by boiling the acid with aniline (5—6 parts), and crystallises from dilute alcohol in colourless plates which blacken at high temperatures.

Phenylhydrazine amidosulphonate, $NH_2 \cdot SO_3 \cdot NH_3 \cdot NHPh$, prepared like the aniline salt, crystallises in large, colourless needles, and melts at 124°. *Ammonium phenylhydrazidosulphonate*,

$$NHPh \cdot NH \cdot SO_3 \cdot NH_4,$$
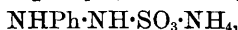
is obtained in a similar manner to the aniline derivative; it crystallises from alcohol in colourless, lustrous, flat needles, melts at 208° with decomposition, and, in aqueous solution, gives a light-grey precipitate with mercuric chloride, and a metallic mirror with silver nitrate. The yield is quantitative.

Ammonium benzeneazosulphonate, $NPh \colon N \cdot SO_3 \cdot NH_4$, is formed by the oxidation of the preceding compound by means of mercuric oxide; it crystallises in yellow plates, or flat needles, and melts and decomposes at 205°. The *potassium* and *sodium salts* crystallise in yellow plates. The *silver salt*, $N_2Ph \cdot SO_3Ag$, is deposited in gold-coloured plates, and explodes on heating. The *ethylic salt* is unstable, and was obtained as a dark-red, viscid liquid. The *free acid* has only been prepared in solution, and readily decomposes. The preceding sulphonic acid derivatives of phenylhydrazine and aniline are probably not formed directly, but are either produced from the salts by the elimination of water and subsequent action of this water on the diamide $NH_2 \cdot SO_3 \cdot NH_3R = NH_2 \cdot SO_2 \cdot NHR + H_2O = NH_4 \cdot SO_3 \cdot NHR$; or they are formed by the elimination of ammonia and its combination with the free sulphonic acid, thus $RNH_2 + NH_2 \cdot SO_3H = RNH \cdot SO_3H + NH_3 = RNH \cdot SO_3 \cdot NH_4$ ($R = C_6H_5$ or $NHPh$). As no intermediate products have been isolated, it is impossible to distinguish between these theories.

J. B. T.

Synthesis of Pentamethylenecarboxylic acid. By W. STAUSS (*Ber.*, **27**, 1228—1230).—The pentamethylenecarboxylic acid, prepared by Gärtner (*Annalen*, **275**, 331) from ketopentamethylene by

means of hydrocyanic acid, can also be obtained by the action of tetramethylene dibromide on ethylic malonate in the presence of sodium ethoxide. The pentamethylenedicarboxylic acid,

$$\begin{matrix}CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2\end{matrix} {>} C(COOH)_2,$$
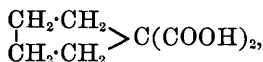
obtained by the hydrolysis of the product, melts at 176—178°, and loses the elements of carbonic anhydride. The monobasic acid thus produced is identical with Gärtner's acid.

Note.—The author has overlooked the fact that Haworth and Perkin (Trans., 1894, 86) have carried out the synthesis of pentamethylenecarboxylic acid in precisely the way indicated in the foregoing paper.   A. H.

Synthesis of Hexahydrobenzoic acid. By H. BUCHERER (*Ber.*, **27**, 1230—1232).—Ketohexamethylene reacts with hydrocyanic acid in a similar manner to ketopentamethylene (*Annalen*, **275**, 333), first the nitrile, and from that by hydrolysis *α-hydroxyhexamethylene-carboxylic acid*, $CH_2 {<}\begin{matrix}CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2\end{matrix}{>}CH(OH) \cdot COOH$, being produced. This substance is soluble in 14 parts of water, readily soluble in alcohol, ether, and benzene, and crystallises in colourless plates, or from aqueous solution in thick prisms with a vitreous lustre, and melts at 106—107°. The *calcium* salt, $C_{14}H_{22}CaO_6 + 3H_2O$, and *silver* salt are both crystalline. When heated at 190—200° with phosphorus and hydriodic acid, the free acid is converted into hexahydrobenzoic acid.   A. H.

Constitution of Benzene. By J. W. BRÜHL (*J. pr. Chem.*, [2], **49**, 201—294, and *Ber.*, **27**, 1065—1083).—The author discusses at length our present views on the constitution of benzene, and concludes that Kekulé's formula, in which three double bonds are supposed to exist in the benzene ring, is in closer agreement with the facts than Claus's diagonal formula which is supported by v. Baeyer (Abstr., 1892, 1211).

Substance.	d at 20°/4°.	Mol. vol. at 20°.	$P\dfrac{n^2-1}{d(n^2+2)}.$	
			For H_a.	For D.
Benzene, C_6H_6	0·8799	88·65	25·93	26·13
Dihydrobenzene, C_6H_8	0·8478	94·36	26·33	26·51
Tetrahydrobenzene, C_6H_{10}	0·8102	101·21	26·87	27·01
Hexahydrobenzene, C_6H_{12}	0·790	107·2	27·56	27·66
Hexane, C_6H_{14}	0·6603	130·25	29·70	29·84
Hexylene, C_6H_{12}	0·6825	128·08	29·45	29·61
Diallyl, C_6H_{10}	0·6880	119·18	28·77	28·96
Dipropargyl, C_6H_6	0·8049	96·91	25·57	25·74

The molecular volumes and refraction constants of benzene, and of several hydrogenated benzenes and six-carbon atoms open-chain hydrocarbons were determined ; the results are tabulated on p. 366.

The numbers obtained for the densities decrease slowly as the degree of hydrogenation of the benzene nucleus increases ; considerable difference exists, however, between the density of hexahydrobenzene and that of hexane. The density slowly increases from hexane to diallyl, and then, in going from diallyl to dipropargyl, a great increase occurs. The molecular volumes change in much the same way. The change in molecular volume which occurs on passing from one hydrocarbon to another is even more marked than the change of density. Large differences in specific refraction also exist between hexahydrobenzene and hexane, and between diallyl and dipropargyl ; the molecular refractions for the rays H_α and D change in an analogous manner, as is seen on inspecting the table. In the complete paper, a table of the molecular and specific dispersions between H_γ and H_α is given, from which it is seen that these constants also exhibit sudden changes at the points mentioned above.

The large changes in physical properties observed on passing from hexahydrobenzene to hexane, and from diallyl to dipropargyl, are evidently due, in the first case, to the opening of the ring, and, in the second, to the change of an ethylenic bond to an acetylenic one. No large change in any of these properties is observed in the passage from benzene to dihydrobenzene, as would be expected if the molecular structure of benzene materially differed from that of its dihydroderivative. The hypothesis that benzene possesses a cyclic or a diagonal constitution, is consequently opposed to the facts, and it must be concluded that benzene contains three ethylenic bonds, dihydrobenzene two, and the tetrahydro-derivative one only. The molecular refractions calculated for all the above hydrocarbons on these assumptions, are in close agreement with those observed. According to v. Baeyer, the benzene nucleus in phthalic acid should contain three diagonal bonds ; the observed molecular refraction of ethylic phthalate is, however, 58·20 for the ray H_a, whilst the value, calculated on v. Baeyer's assumption, is only 51·79. The value calculated from the Kekulé formula is 57·30, a number which agrees fairly well with that observed. Benzene and phthalic acid are, consequently, not representatives of a desmotropic ring system, and the benzene nucleus cannot exist in two tautomeric forms, but always has the constitution indicated by the Kekulé formula.

The author considers that the thermochemical data for benzene derivatives, obtained by Stohmann (this vol., ii, 80), and supposed by him to be evidence strongly supporting the views of v. Baeyer, are in complete accordance with Kekulé's benzene formula. Stohmann's work, and also that of v. Baeyer, is discussed at length.

The arrangement in space of the atoms constituting the benzene molecule is best grasped by the use of Sachse's models.

W. J. P.

New Mode of Formation of Nitrosobenzene. By E. BAMBERGER and B. BERLÉ (*Ber.*, **27**, 1182).—It has hitherto been stated,

that when azoxybenzene is heated, aniline and azobenzene are pro-
duced. The authors find that if the heating is carried out slowly,
small quantities of nitrosobenzene are also formed. 　　　L. T. T.

**Action of Sulphuryl Chloride on the Phenols and their
Ethers.** By A. PERATONER and F. FINOCCHIARO (*Gazzetta*, **24**, i,
236—246; compare Töhl and Eberhart, this vol., i, 132).—The
authors confirm Dubois' statement (*Zeits. Chem.*, 1866, 705) that
parachlorophenol is the only product of the action of sulphuryl
chloride on phenol, either solid or in chloroform solution.

Sulphuryl chloride has no action on boiling anhydrous ethereal
solutions of phenylic benzoate, dibenzoylresorcinol, or triacetylphloro-
glucinol, although in the latter case a little free phloroglucinol is
formed, probably owing to the presence of moisture. On boiling an
anhydrous ethereal solution of diacetylresorcinol with sulphuryl
chloride, a small quantity of a derivative containing chlorine in the
acetyl-group is obtained; its nature could not be more exactly de-
termined.

Trichlorophloroglucinol is obtained by the action of sulphuryl
chloride on phloroglucinol in ethereal solution; it melts at 133—134°,
not at 129° as stated by Hazura and Benedikt (Abstr., 1886, 52).
　　　　　　　　　　　　　　　　　　　　　　　　　　　W. J. P.

Action of Halogens on Homocatechol. By H. COUSIN (*Compt.
rend.*, **118**, 809—811).—When chlorine is passed into a solution of
homocatechol in glacial acetic acid until it begins to acquire a red
colour, *trichlorohomocatechol*, $C_7H_5Cl_3O_2$, is formed, and crystallises
from dilute acetic acid containing a small quantity of sulphurous acid
in slender, white needles, which rapidly become brown on exposure
to light. It is insoluble in water, but dissolves in alcohol, ether, and
boiling acetic acid. The crystals are hydrated, but lose their water
in a dry vacuum, and the anhydrous compound melts at 179—180°.

Longer action of chlorine on the acetic acid solution of homocatechol
yields a dark red solution, which, on cooling, deposits bright red,
crystalline lamellæ of the compound $C_7H_3Cl_3O_2$, a dehydration product
analogous to that obtained by Zincke from tetrachlorocatechol. The
same product is obtained by the action of a mixture of concentrated
nitric acid and glacial acetic acid on a solution of trichlorohomo-
catechol in a small quantity of absolute alcohol. It can be recrystal-
lised from hot acetic acid, and also dissolves in alcohol and ether, but
is insoluble in water; it melts at 97—98°.

The prolonged action of chlorine yields pale yellow, higher chlorine
derivatives, which have not yet been fully investigated.

When bromine is added gradually to homocatechol until it is no
longer absorbed, there is an energetic action, and when the product
is repeatedly crystallised from acetic acid containing a small quantity
of sulphurous acid, the *tribromo*-derivative, $C_7H_5Br_3O_2$, is obtained in
long, silky, white needles, which become brown when exposed to
light; it melts at 162—164°, and is insoluble in water, but dissolves
in alcohol, ether, and acetic acid. With excess of bromine, homo-
catechol yields a red product, analogous to the chlorine compound; it
is more easily obtained by the action of nitric acid, and crystallises

from hot acetic acid in large, garnet-red lamellæ, which melt at 117—118°. When dissolved in alcohol and heated with sulphurous acid, the compound $C_7H_5Br_3O_2$ is regenerated.

Prolonged action of bromine on homocatechol yielded no substitution products higher than the tribromo-derivative.

Iodine, under various conditions, yields no iodo-derivatives with homocatechol. C. H. B.

Derivatives of Orthoamidobenzylic Alcohol. By C. Paal and H. Senninger (*Ber.*, **27**, 1084—1087).—The authors have continued the investigation (Abstr., 1893, i, 23) of orthoamidobenzylic alcohol and its derivatives. The alcohol yields orthotoluidine on reduction with metallic sodium in alcoholic solution, and gives saligenin when treated with nitrous acid.

Orthoamidobenzylic alcohol hydrogen oxalate, $C_7H_9NO,H_2C_2O_4$, crystallises in white needles, melting at 130°, and is soluble in water or hot alcohol. The *picrate*, $C_7H_9NO,C_6H_3N_3O_7$, is obtained in slender, yellow needles, melting at 110°.

Diazobenzylic alcohol hydrogen sulphate, $OH \cdot CH_2 \cdot C_6H_4 \cdot N_2 \cdot HSO_4$, is obtained by diazotising the alcohol in the ordinary way with amylic nitrite and sulphuric acid; it crystallises in greenish needles, exploding at 50°, and is readily soluble in water. On diazotising the alcohol with sodium nitrite and hydrochloric acid, and adding a soda solution of resorcinol, the *sodium*-derivative of resorcinolorthoazobenzylic alcohol is obtained in red, microcrystalline flocks. The free *azo*-compound, $C_6H_3(OH)_2 \cdot N_2 \cdot C_6H_4 \cdot CH_2 \cdot OH$, crystallises in red needles, melting at 170°. The *α-naphtholazo*-compound crystallises in leaflets melting at 182°, whilst the *β-naphtholazo*-compound is obtained in brown needles, melting at 185°. Similar compounds with phenol and dimethylaniline were prepared, although not in a pure state.

On boiling orthoamidobenzylic alcohol with epichlorhydrin, a *chlorohydroxypropylamidobenzylic alcohol*, $C_{10}H_{14}ClNO_2$, is obtained; it forms white needles, melting at 95°, and is readily soluble in the ordinary organic solvents. W. J. P.

Relationships between Nitrosamines, Diazo-acids, and Isodiazo-compounds. By E. Bamberger (*Ber.*, **27**, 1179—1182).—The direct conversion of isodiazo-salts into nitrosamines of secondary bases has been recently effected (Schmitt and Schraube, this vol., i, 237, and Bamberger, *ibid.*, 295). The author has now succeeded in reversing this action. Methylphenylnitrosamine, when dropped on to fused potash, is rapidly oxidised, with formation of isodiazobenzene. Similarly, β-naphthylnitrosamine and benzylmethylnitrosamine yield the corresponding isodiazo-salts. Benzenediazoic acid, when treated with 8 per cent. sodium amalgam, is partially reduced to isodiazobenzene. L. T. T.

Action of Diazobenzene Chloride and its Homologues on Ethylic Cyanacetate. By F. Krückeberg (*J. pr. Chem.*, [2], **49**, 321—354; compare Abstr., 1893, i, 210, 509).—The ethylic salts of azo-aromatic cyanacetic acids can be obtained in a stable (β) and an

unstable (α) modification. The former is produced when the aqueous solution of the potassium compound is decomposed by carbonic anhydride, the latter when a mineral acid or acetic acid is used to effect the decomposition. The α-form generally passes into the β-form when heated either alone or in alcohol.

Ethylic carboxyethylazobenzenecyanacetate (Abstr., 1893, i, 509) crystallises in white needles and melts at 107°; when warmed with alcoholic potash, the carboxethyl group is replaced by potassium. *Ethylazobenzenecyanacetamide*, $N_2Ph \cdot CEt(CN) \cdot CONH_2$, is the product of the action of alcoholic ammonia on ethylic ethylazobenzenecyanacetate; it is nearly colourless, and melts at 155°. The benzoyl (Abstr., 1893, i, 210) and carboxethyl derivatives yield *azobenzenecyanacetamide* (m. p. 245°, *loc. cit.*) under similar treatment.

Azobenzeneacetamide, $N_2HPh \cdot CH \cdot CO \cdot NH_2$, is the product of the action of aqueous potash on ethylic azobenzencyanacetate; it crystallises in yellowish needles, and melts at 178°. The corresponding acid is identical with Elber's phenylhydrazineglyoxylic acid (Abstr., 1885, 535).

By passing nitrous anhydride into a cooled benzene solution of either α- or β-ethylic azobenzenecyanacetate, a compound, apparently $N_2HPh \colon C(CN) \cdot COOEt, N_2O_3$, is obtained in white crystals, which soon become brown in air, and explode at 70°. This substance does not give Liebermann's reaction, and phenol is a product of its distillation with water. When alcohol or ether is used as the solvent, this compound is not produced. If, during the passage of the nitrous anhydride through the benzene solution, the temperature rises to that of the room, a different compound, possibly $NO \cdot NPh \cdot N \colon C(CONH_2) \cdot COOEt$, is formed; this crystallises in slender, green needles, melts at 178°, and dissolves freely in benzene, but only sparingly in ether, light petroleum, or water; it does not give Liebermann's reaction.

Iodine in aqueous solution converts α-ethylic azobenzenecyanacetate into the β-modification. Bromine yields a *dibromo*-derivative, which crystallises in laminæ, melts at 166°, and dissolves freely in benzene, glacial acetic acid, and alcohol, more sparingly in ether and light petroleum, but not in water.

Ethylic α-azorthotoluenecyanacetate (Abstr., 1893, i, 509) crystallises in yellow rhombohedra, melts at 85°, and dissolves to the extent of 24·57 parts in 100 of benzene at 19°. It is readily transformed into the more stable β-form when heated above its melting point. The β-modification melts at 133°, and dissolves to the extent of 5·7 parts in 100 of benzene at 19°. Thus the higher melting point and lower solubility belong to the stable form of the orthotoluene derivative, but to the unstable form of the benzene derivative. By hydrolysis with alcoholic potash, the ethylic salt yields the corresponding *acid*, which decomposes and melts at 173°.

Ethylic α-azoparatoluenecyanacetate (*loc. cit.*) melts at 116—118°; 9·74 parts of it dissolve in 100 of benzene at 20°. The β-modification melts at 74—75°, and dissolves in benzene at 20° to the extent of 53·65 parts in 100.

Ethylic azometaxylenecyanacetate, $C_6H_3Me_2 \cdot N_2 \cdot CH(CN) \cdot COOEt$. The stable β-form crystallises in yellow prisms and melts at 166°; 3·61

parts dissolve in 100 of benzene at 18°. The unstable α-form crystallises in yellow prisms, melts at 74—75°, and dissolves to the extent of 25·00 parts in 100 of benzene at 18°.

Ethylic azopseudocumenecyanacetate, from diazopseudocumene chloride and ethylic cyanacetate. The β-form melts at 136°, the α-form at 100°; both forms are freely soluble in alcohol, ether, and benzene, and crystallise in slender needles. The corresponding *acid* crystallises in long prisms, and melts at 184°.

Ethylic carboxyphenylhydrazonecyanacetate,

$$COOH \cdot C_6H_4 \cdot N_2H \colon C(CN) \cdot COOEt,$$
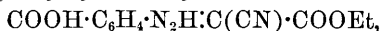
from ethylic cyanacetate and diazobenzene hydrochloride, crystallises in slender needles and melts at 215°.

Formulæ are given, showing how the α- and β-modifications of these ethylic salts may be (1) stereoisomerides, (2) tautomerides, or (3) isomerides formed by migration of a hydrogen atom.　　A. G. B.

Acetoacetanilide. By L. KNORR and B. REUTER (*Ber.*, **27**, 1169—1177).—*Acetoacetanilide* is prepared by the interaction of ethylic acetoacetate and aniline at 130—140° and crystallises from water in colourless plates melting at 85°. The yield is more than one-third of the theoretical. The *oxime*, $NOH \colon CMe \cdot CH_2 \cdot CO \cdot NHPh$, is formed at ordinary temperatures, crystallises from alcohol in needles, and melts at 125°. It is readily soluble in alkalis, insoluble in dilute acids, and gradually decomposes spontaneously. On heating with glacial acetic acid, or soda, or by the action of sulphuric acid, the oxime is converted into methylisoxazolone, $CMe<^{N-O}_{CH_2 \cdot CO}$ (compare Hantzsch, Abstr., 1891, 739).

The *dioxime*, $NOH \colon CMe \cdot C(NOH) \cdot CO \cdot NHPh$, is prepared by gently heating the oxime with hydroxylamine hydrochloride, and crystallises from alcohol in yellow plates melting at 192°. It readily dissolves in alkalis, is precipitated by acids, and on heating with phenylhydrazine in acetic acid solution, 1-phenyl-3-methyl-4-keto-5-pyrazolone phenylhydrazone, $CMe<^{N-----NPh}_{C(N \cdot NHPh)}>CO$, is formed; this compound is obtained in a similar manner from methylketoisoxazolone phenylhydrazone (see below), diphenylhydrazineacetylglyoxalic acid being formed in both cases as an intermediate product.

Acetoacetanilide ketophenylhydrazone, $NHPh \cdot N \colon CAc \cdot CO \cdot NHPh$, is prepared by the action of diazobenzene chloride on acetoacetanilide; it crystallises from alcohol in pale yellow needles, and melts at 98—99°.

Acetoacetanilide phenylhydrazone, $NHPh \cdot N \colon CMe \cdot CH_2 \cdot CO \cdot NHPh$, is formed from phenylhydrazine and the anilide; it crystallises from alcohol in plates, melts at 128°, and gives an intense cherry colour with sulphuric acid. The yield is 75 per cent. of the theoretical. On boiling with soda or glacial acetic acid, it is converted into 1-phenyl-3-methyl-5-pyrazolone, which was identified by the formation of pyrazole-blue.

Acetylglyoxalanilide diphenylhydrazone,

$$NHPh \cdot N\mathpunct{:}CMe \cdot C(N \cdot NHPh) \cdot CO \cdot NHPh,$$

from the phenylhydrazone by the action of diazobenzene chloride or from phenylhydrazine and the ketohydrazone, crystallises from alcohol in needles, melts at 173—175°, and, on heating with glacial acetic acid, is converted into methylketopyrazolone phenylhydrazone (see preceding page).

Acetylglyoxalanilide oximephenylhydrazone,

$$NHPh \cdot N\mathpunct{:}CMe \cdot C(NOH) \cdot CO \cdot NHPh,$$
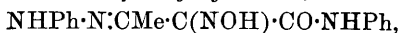
is prepared from the isonitroso-derivative and phenylhydrazine, and crystallises, with 1 mol. alcohol, in yellow needles melting at 181°, the alcohol-free compound melts at 168—169°. On boiling with glacial acetic acid, it is converted into 1-phenyl-3-methyl-4-isonitroso-

5-pyrazolone, $CMe\begin{smallmatrix} N\text{------}NPh \\ \diagdown \\ C(NOH) \cdot CO \end{smallmatrix}$.

Acetylglyoxalanilide phenylhydrazoneoxime,

$$NOH\mathpunct{:}CMe \cdot C(N \cdot NHPh) \cdot CO \cdot NHPh,$$

is formed from the ketohydrazone and hydroxylamine hydrochloride; it crystallises from alcohol in thin plates, and melts at 175° with decomposition.

By the interaction of diazobenzene chloride and acetoacetanilide oxime or on methylisoxazolone, *ketomethylisoxazolone phenylhydrazone,*

$CMe\begin{smallmatrix} N\text{------}O \\ \diagdown \\ (N \cdot NHPh) \cdot CO \end{smallmatrix}$, is produced; it is also formed by the action of nitrous acid on the oxime, and by the hydrolysis of acetylglyoxalanilide hydrazoneoxime; it crystallises from alcohol in yellow plates, melts and decomposes at 189°, and, on treatment with phenylhydrazine, is converted into acetylglyoxalic acid diphenylhydrazone, $NHPh \cdot N\mathpunct{:}CMe \cdot C(N \cdot NHPh) \cdot COOH$ (m. p. 212°). Phenylmethylisotriazolecarboxylic acid, $CMe\begin{smallmatrix} N\text{--}NPh \\ \diagdown \\ C(COOH) \end{smallmatrix}\!\!\gg\!N$, has been previously prepared by Pechmann, and is obtained by heating acetylglyoxalanilide oximehydrazone with potash at 140—150°, acetylglyoxalic acid hydrazoneoxime is formed as an intermediate product.

J. B. T.

Action of Picrylic Chloride on Hydrazine Hydrate. By A. PURGOTTI (*Gazzetta,* **24,** i, 112—116).—*Picrylhydrazine,*

$$C_6H_2(NO_2)_3 \cdot NH \cdot NH_2 \; [= 1 : 3 : 5 : 6],$$

is obtained by boiling a mixture of caustic potash, hydrazine sulphate, and picrylic chloride in alcoholic solution; water must be present in order that the yield of the product should be good. It crystallises in brown, transparent, monosymmetric crystals, and melts and decomposes at 173°. It is soluble in ethylic acetate; it reduces Fehling's solution and ammoniacal silver nitrate. On boiling with benzaldehyde, it yields a golden-yellow, crystalline *substance* melting at 252°.

W. J. P.

Reduction of Nitro-compounds. By E. BAMBERGER (*Ber.*, **27**, 1347—1350).—The author finds that when nitrobenzene is boiled for a short period with water and zinc dust, *β-phenylhydroxylamine*, NHPh·OH, separates from the filtrate in long, colourless needles; it melts at 80—81°, and is characterised by its sensitiveness towards alkalis, which instantaneously decompose it, as well as by its great reducing power. It is readily converted into nitrosobenzene on oxidation, and into paramidophenol by mineral acids. Nitromethane when boiled with zinc dust and water, yields methylhydroxylamine without recognisable quantities of methyamine or ammonia; in a similar manner, nitric acid and nitrous acid yield not inconsiderable amounts of hydroxylamine on reduction with zinc dust and water. (Compare, however, Wohl, *Ber.*, **27**, 1432; Bamberger, *ibid.*, 1547.)

A. R. L.

Blue Coloration Produced by the Action of Acids on Leuc-auramines. By A. ROSENSTIEHL (*Compt. rend.*, **118**, 741—743).— Graebe observed that when leucoauramine is treated with acids, a blue coloration is produced, and he assumed that this compound is capable of existing in two isomeric modifications, one colourless, the other coloured. The coloration is fugitive with hydrochloric acid but permanent with acetic acid. The author has observed, however, that a precisely similar coloration is obtained by the action of acids on diamidotetramethylbenzhydrol, which has a constitution similar to that of leucauramine. If the group ·C_6H_4·NMe_2 is represented by A, leucauramine is A_2:CH·NH_2, whilst diamidotetramethylbenzhydrol is A_2:CH·OH.

If leucauramine prepared by Graebe's method is dissolved in dilute hydrochloric acid, heated for 30 minutes on a water bath, and made alkaline with sodium hydroxide, a crystalline precipitate is obtained which contains 90 per cent. of diamidotetramethylbenzhydrol and 10 per cent. of unaltered leucauramine. When the benzhydrol is treated with an insufficient quantity of acid, the principal product is A_3:CH, the leuco-base of hexamethylated Paris violet.

Leucauramine does not exist in the form of a blue modification, as Graebe supposed; the blue coloration is due to the formation of the chlorhydrin of diamidotetramethylbenzhydrol.

C. H. B.

Amidoguanidine and its Alkyl-derivatives. By G. PELLIZZARI and G. CUNEO (*L'Orosi*, **17**, 73—89).—Amidoguanidine (compare Thiele, Abstr., 1892, 1295) may be prepared by heating cyanamide with hydrazine hydrochloride in alcoholic solution.

Orthotolylamidoguanidine hydrochloride,

$$C_7H_7·NH·NH·C(NH)·NH_2,HCl,$$
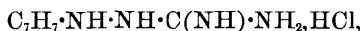
is obtained by heating a mixture of orthotolylhydrazine hydrochloride and cyanamide or of phenylhydrazine hydrochloride and guanidine carbonate in alcoholic solution; it crystallises in large, red prisms and melts at 212°. The *nitrate* is obtained in beautiful, colourless needles melting at 206·5°; the *platinochloride* forms magnificent yellow needles, and the *picrate* crystallises in large, yellow needles melting at 206°.

Paratolylhydrazine hydrochloride and cyanamide interact with formation of *paratolylamidoguanidine hydrochloride;* this crystallises in transparent scales and melts at 196·5°. The *nitrate* is obtained in transparent laminæ melting at 181°, and the *platinochloride* forms beautiful, red crystals; the *picrate* crystallises in needles melting at 212°.

α-Naphthylamidoguanidine hydrochloride,

$$C_{10}H_7 \cdot NH \cdot NH \cdot C(NH) \cdot NH_2, HCl,$$
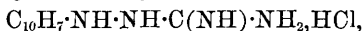
prepared by the action of cyanamide on α-naphthylhydrazine hydrochloride, separates from its aqueous solution in colourless crystals melting at 166°; the platinochloride is a yellow, crystalline powder.

β-Naphthylamidoguanidine hydrochloride is obtained in minute, reddish crystals, which decompose at 250—260°; the *nitrate* is similar in appearance and melts at 230°. The *platinochloride* and *picrate* are coloured, crystalline powders.

The bases whose salts are described above, could not be obtained in the free state; their salts immediately reduce ammoniacal silver nitrate but do not react with benzaldehyde.

Ethylphenylamidoguanidine hydrochloride,
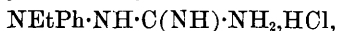
$$NEtPh \cdot NH \cdot C(NH) \cdot NH_2, HCl,$$

is obtained by boiling a mixture of α-ethylphenylhydrazine hydrochloride and cyanamide in alcoholic solution. The *platinochloride* forms a flocculent precipitate and melts and decomposes at 150°, whilst the *picrate* crystallises in hard, red prisms melting at 224°, and is accompanied by a small proportion of another *picrate* which separates in transparent scales melting at 269°.

Phenylamidomethylguanidine hydrochloride,

$$NHPh \cdot NMe \cdot C(NH) \cdot NH_2, HCl,$$
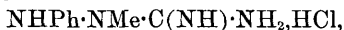
is prepared by the interaction of cyanamide and β-phenylmethylhydrazine hydrochloride in boiling alcoholic solution; it crystallises in small, colourless prisms and melts at 227°. The *platinochloride* crystallises in transparent, red needles, and the *nitrate* separates in white crystals melting at 105—106°; the picrate crystallises in yellow needles melting and decomposing at 215°.   W. J. P.

Ethylic Benzalbiuretamidocrotonate and Benzalbiuret. By P. BIGINELLI (*Gazzetta*, **24**, i, 291—295).—The author has previously shown (Abstr., 1893, i, 645) that carbamide interacts with an aldehyde and an acetoacetate or oxalacetate, water being eliminated, and a compound of the following type being formed,

$$CO<\begin{matrix}NH \cdot CR'' \cdot C \cdot COOEt \\ NH \text{——} CHR\end{matrix};$$
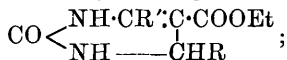
it is now shown that a similar action occurs if other amides, such as biuret, are substituted for carbamide.

On boiling a mixture of biuret hydrate, benzaldehyde, and ethylic acetoacetate with absolute alcohol, or on heating the mixture alone at 170°, water is formed, and a *substance* of the composition $C_{15}H_{19}N_3O_5$ separates on cooling. It crystallises in tufts of small needles, melt-

ing at 184—185°, is soluble in hot alcohol, does not give the general reactions for biuret, and is hydrolysed by dilute acids or alkalis with liberation of benzaldehyde. It probably has the constitution

$$\begin{array}{l}\text{CHPh·NH·CO—NH}\\ \quad |\qquad\qquad\qquad\quad\,\,\rangle\text{CO,H}_2\text{O.}\\ \text{C(COOEt)·CMe·NH}\end{array}$$

Ethylic benzalbiuretamidocrotonate may be prepared by the general method described in the paper referred to above; it therefore became of interest to attempt the preparation of compounds of biuret with aldehydes. On heating benzaldehyde with biuret hydrate at 170°, a product is obtained from which *benzalbiuret*, $\text{NH}<^{\text{CO·NH}}_{\text{CO·NH}}>\text{CHPh}$, may be isolated by washing with alcohol and water; it crystallises in small pyramids melting and decomposing at 272—273°, and is soluble in hot alcohol. It is not hydrolysed by dilute acids or alkalis in the cold, but, on boiling with concentrated potash, benzaldehyde is formed; ethylic acetoacetate has no action on it at 180°.

W. J. P.

Action of Aromatic Orthodiamines on some Anhydrides of Bibasic acids. By F. ANDERLINI (*Gazzetta*, **24**, i, 140—150).— Orthophenylenediamine and succinic anhydride in cold benzene solution yield an additive *product*, $C_6H_4(NH_2)_2,C_4H_4O_3$, as a white deliquescent amorphous powder, which decomposes at 80°. On boiling with benzene or absolute alcohol, it decomposes with formation of *orthophenylenesuccinyldiimide*, $C_6H_4<^{\text{NH·CO}}_{\text{NH·CO}}>C_2H_4$; this crystallises in pearly scales melting and decomposing at 237°, and is soluble in alcohol or hot water.

Orthophenylenediamine combines with maleïc anhydride in benzene solution to form an additive *product*, $C_{10}H_{10}O_6N_2$, which separates from hot alcohol in small yellow, lustrous crystals melting and decomposing at 124—125°. On boiling with absolute alcohol, it yields a yellow, crystalline condensation *product* of complex composition melting and decomposing at 240°; another crystalline *product* melting at 168° is also formed.

The additive *product*, $C_6H_4(NH_2)_2,C_8H_4O_3$, of orthophenylenediamine and phthalic anhydride, separates from hot alcohol as a yellow, crystalline mass melting at 144—155°. It yields *orthophenylenephthalyldiimide*, $C_6H_4<^{\text{NH·CO}}_{\text{NH·CO}}>C_6H_4$, when boiled with absolute alcohol; this crystallises in white needles melting and decomposing at 278°, and is insoluble in water.

The additive *product*, $C_6H_3Me(NH_2)_2,C_4H_4O_3$, obtained from orthotolylenediamine and succinic anhydride, is a hygroscopic, amorphous mass which decomposes at 90°; on heating at 100°, it yields *orthotolylenesuccinyldiimide*, $C_6H_3Me<^{\text{NH·CO}}_{\text{NH·CO}}>C_2H_4$, which crystallises in pearly-white scales melting and decomposing at 185—186°; it is soluble in hot water.

Orthotolylenediamine and maleïc anhydride yield an additive *product*, $C_6H_3Me(NH_2)_2,C_4H_2O_3$, but the condensation product could not be isolated.

The additive *product* of orthotolylenediamine and phthalic anhydride, $C_6H_3Me(NH_2)_2,C_8H_4O_3$, is a crystalline powder which decomposes at 90°. On boiling its benzene solution, *orthotolylenephthalyldiimide*, $C_6H_3Me{<}^{NH·CO}_{NH·CO}{>}C_6H_4$, is deposited; it forms a yellow, crystalline mass which softens at 140°.   W. J. P.

Ethylic Phenyloxalacetate and Phenylmalonic acid. By W. WISLICENUS (*Ber.*, **27**, 1091—1095; compare this vol., i, 323).— Ethylic phenyloxalacetate, $COOEt·CO·CHPh·COOEt$, was prepared in the manner described for the oxalacetate (Abstr., 1888, 361). Its colourless *sodium* and green *copper derivatives* were prepared. From the former, by the action of dilute sulphuric acid, the ethylic salt itself was set free as a colourless oil; it was distilled under diminished pressure, when *ethylic phenylmalonate* was formed; the latter was purified by fractionation under diminished pressure. It is a colourless, odourless oil, boiling with slight decomposition at 285°; under 14 mm. pressure, it boils at 170—172°. *Phenylmalonic acid*, $CHPh(COOH)_2$, melts at 152—153°, with evolution of carbonic anhydride and formation of phenylacetic acid. Its *sodium, calcium, silver*, and blue *copper* ($5H_2O$) *salts* were prepared.   C. F. B.

Action of Heat on Ethylic Dibenzoylsuccinate. By L. KNORR and M. SCHEIDT (*Ber.*, **27**, 1167—1168).—Ethylic dibenzoylsuccinate is prepared in a similar manner to ethylic diacetosuccinate (compare this vol., i, 360); on heating at 270—290°, alcohol is eliminated, and a compound, $C_{18}H_{10}O_4$, is formed which is sparingly soluble, crystallises from ethylic acetoacetate in needles, melts at 288—289°, and sublimes without decomposition. It dissolves in concentrated sulphuric acid with a blue-violet colour; the yield is small. The compound appears to be a quinone, and although its constitution is uncertain, it is probably represented by one of the formulæ $C_6H_4{<}^{CO·CH·CO}_{CO·CH·CO}{>}C_6H_4$;

$C_6H_4{<}^{C(OH)·C·CO}_{C(OH)·C·CO}{>}C_6H_4$; $C_6H_4{<}^{CO{-}{-}C{:}C(OH)}_{C(OH){:}C·CO{-}{-}{-}}{>}C_6H_4$. The mother liquor yields *bisdiphenylpyrazolone*,

$$NPh{<}^{N{=}CPh\quad CPh{:}N}_{CO·C{=}{=}C{-}CO}{>}NPh,$$
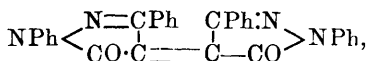
which melts at 320° with decomposition, readily dissolves in alkalis, and is converted into a pyrazolone-blue on oxidation. Dibenzoylethane (diphenacyl) is formed from ethylic dibenzoylsuccinate by warming it with soda (3 per cent.), or by heating with water at 150—170°, or with alcohol at 250°.   J. B. T.

Action of Hydrogen Sulphide on Sulphones. Influence of Solvents on Chemical Change. By R. OTTO (*J. pr. Chem.*, [2], **49**, 378—391; compare Abstr., 1893, i, 344).—Benzenesulphonic chloride is reduced by hydrogen sulphide in aqueous alcohol, with

greater difficulty in ether, particularly in absence of water; the reduction is still more difficult in methylic alcohol, benzene, or acetic acid.

The following are reducible by hydrogen sulphide in aqueous ether:—Paratoluenesulphonic chloride, α- and β-naphthalenesulphonic chloride, sulphobenzidemetabenzenedisulphonic chloride, and sulphobenzidemetasulphonic chloride. In aqueous alcohol, parabromobenzenesulphonic chloride and sulphobenzidemetadisulphonic chloride are reducible. Paratoluenesulphonic chloride cannot be reduced in benzene.

Phenylic thiobenzenesulphonate is reduced in anhydrous methylic alcohol, and in aqueous alcohol, but not in benzene. Ethylic benzenesulphinate is reducible alone. Benzenesulphinic acid is reduced in aqueous alcohol, anhydrous methylic alcohol, and in water; β-naphthalenesulphinic acid is reduced in anhydrous methylic alcohol, and in chloroform, but with difficulty in benzene.

Monosulphones, ethylenediphenylsulphone, ethylic paratoluenesulphonate and ethylic benzenesulphonate cannot be reduced.

β-Naphthylic bisulphide melts at 139°, not 132°.   A. G. B.

The Carboxybenzilehydrazones. By K. AUWERS and A. CLOS (*Ber.*, **27**, 1133—1140).—If benzile (1 mol.) is digested on the water bath with parahydrazinebenzoic acid (1 mol.), *benzilemono-hydrazoneparacarboxylic acid*, $CPhO\cdot CPh:N_2H\cdot C_6H_4\cdot COOH$, is formed; but with more of the latter (2 mols.), *benziledihydrazoneparadicarboxylic acid*, $C_2Ph_2(N_2H\cdot C_6H_4\cdot COOH)_2$ is obtained. These are both yellow crystalline substances, and melt respectively at 212° and above 320°, with decomposition. If benzile-α-monoxime is heated for 24 hours at 100° with parahydrazinebenzoic acid in absolute alcoholic solution, *benzileoximehydrazoneparacarboxylic acid*, $NOH:CPh\cdot CPh:N_2H\cdot C_6H_4\cdot COOH$, is formed, melting at 249—250°; the β-oxime yields no such compound. (For similar indifferent behaviour of the β-oxime, compare Abstr., 1893, i, 354.) The *monacetyl derivative* of this acid melts at 176°, the *ethylic salt* at 226°. When the acid is heated for 12 hours at 140° with absolute alcohol containing a little hydrochloric acid, *ethylic triphenylosotriazoneparacarboxylate*, melting at 99°, is obtained; the corresponding *acid*,

$$\begin{matrix} CPh:N \\ | \\ CPh:N \end{matrix}\!\!\!>\!N\cdot C_6H_4\cdot COOH, \text{ melts at } 258°.$$ The ethylic salt is more conveniently prepared by heating benzilemonhydrazoneparacarboxylic acid (5 parts) with hydroxylamine hydrochloride (1 part) and absolute alcohol (4 parts) for 16—20 hours at 100°. In both cases, some *diethylic benziledihydrazoneparacarboxylate* is formed at the same time; it melts at 229°. This substance can only be prepared from the corresponding acid with great difficulty; it is necessary to treat the acid with the theoretical quantity of sodium ethoxide in alcoholic solution, add a little water, and heat with ethylic iodide in a tube at 100°.

Some ortho-compounds were prepared in the same way as the above-mentioned para-derivatives. *Benzilemonhydrazoneorthocarboxylic* and *benziledihydrazoneorthodicarboxylic acids* are yellow,

crystalline substances, melting at 212° and above 320 respectively. *Benzileoximehydrazoneorthocarboxylic acid* is colourless, and melts at 226°. In connection with the preparation of these substances, it was noticed that benzile and orthohydrazinebenzoic acid, when heated together at 120° in absolute alcoholic solution, yield E. Fischer's orthohydrazinebenzoic anhydride, $C_6H_4{<}{\substack{NH \\ CO}}{>}NH$. When benzile-oximehydrazoneorthocarboxylic acid is warmed with acetic anhydride, a yellowish substance is formed, which has the formula, $C_9H_8N_2O_2$, and is possibly a monacetyl derivative of the above anhydride.

A series of corresponding meta-compounds can also be obtained, but their preparation is difficult and the yield small, owing to the formation of resinous products.   C. F. B.

Action of Ethylic Oxalate on Dibenzyl Ketone. By L. CLAISEN (*Ber.*, **27**, 1353—1354).—Dieckmann (this vol., i, 324) has shown that ethylic glutarate interacts with ethylic oxalate forming a derivative of diketopentamethylene. One of the author's students showed (Ewan, *Diss. München*, 1890), that *diphenyltriketo-pentamethylene* (oxalyldibenzyl ketone), $CO{<}{\substack{CHPh\cdot CO \\ CHPh\cdot CO}}$, is formed by treating dibenzyl ketone with ethylic oxalate in presence of sodium ethoxide. This compound undergoes isomeric change when heated above its melting point; the product seems to be a hydroxy-lactone, but the experimental evidence as to the mechanism of the change is not yet complete.   A. R. L.

Sulphonation in the Naphthalene Series. By O. DRESSEL and R. KOTHE (*Ber.*, **27**, 1193—1210).—The following researches, undertaken for technical purposes, show that the rule proposed by Armstrong and Wynne (*Proc.*, 1890, 130), according to which a sulphonic-group never enters the naphthalene molecule in the ortho-, peri-, or para-position to a similar group originally present, is liable to some exceptions.

Sulphonation of 2-naphthylamine-2'-sulphonic acid. This substance when sulphonated by means of fuming acid (25 per cent. SO₃) in the cold yields three sulphonic acids, the potassium salts of which separate from aqueous solution in the following order.

*2-Naphthylamine-*1 : 2'-*disulphonic acid.* The *potassium* salt,

$$C_{10}H_5(NH_2)(SO_3K)_2 + 3H_2O,$$

crystallises extremely well, whilst the *hydrogen potassium* salt forms indistinct, slender needles. When its diazo-derivative is converted into the hydrazine, and the latter is oxidised with copper sulphate, and converted into the sodium salt, sodium naphthalene-1 : 2'-di-sulphonate is obtained.

2-Naphthylamine-4 : 2'-disulphonic acid forms a hydrogen sodium salt which crystallises with 1H₂O, and a barium salt which is sparingly soluble in cold water and crystallises in crusts made up of

prisms. This acid has been previously prepared by Schultz, and others.

2-Naphthylamine-4' : 2'-disulphonic acid has been previously described by Armstrong and Wynne (*Proc.*, 1890, **11**). The product of the sulphonation of 2-naphthylamine-2'-sulphonic acid consists of about 50 per cent. of the last named acid, together with about 25 per cent. of each of the other two.

Sulphonation of 2-Naphthylamine-3 : 2'-disulphonic acid. This acid, the preparation of which is the subject of a German patent (46,711), and of which the constitution has been determined by Armstrong and Wynne (*Proc.*, 1890, 127), forms a hydrogen sodium salt which requires 50 parts of cold water to dissolve it. The normal sodium salt is more readily soluble, whilst the hydrogen barium salt is very sparingly soluble indeed. When this acid is sulphonated at the temperature of the water bath, the sole product is 2-naphthylamine-1 : 3 : 2'-trisulphonic acid, but when this or the original disulphonic acid is heated at 130° with fuming sulphuric acid, a change occurs and two new trisulphonic acids accompanied by a tetrasulphonic acid are produced.

*2-Naphthylamine-*1 : 3 : 2'*-trisulphonic acid* forms a *hydrogen sodium* salt of the formula, $NH_2 \cdot C_{10}H_4(SO_3H)(SO_3Na)_2 + 4H_2O$, which crystallises in colourless plates and is readily soluble in water. When the acidified solution of one of the salts of this acid is boiled, the sulphonic group in the position 1 is removed in the form of sulphuric acid, and the original naphthylaminedisulphonic acid is regenerated, a reaction which is common to all the sulphonic acids of 2-naphthol and 2-naphthylamine which contain a sulphonic group in the position 1. The constitution also follows from the fact that this trisulphonic acid can be obtained by heating 2-naphthol-1 : 3 : 2'-sulphonic acid with ammonia.

*2-Naphthylamine-*3 : 3' : 2'*-trisulphonic acid*, obtained by heating the foregoing acid with fuming sulphuric acid at 130°, is separated from the isomeric acid which accompanies it by means of its less soluble *hydrogen sodium* salt. It can be converted by means of the hydrazine reaction into naphthalene-2 : 3 : 3'-trisulphonic acid.

*2-Naphthylamine-*3 : 4' : 2'*-trisulphonic acid*, which accompanies the foregoing compound, forms a *hydrogen sodium* salt which is moderately soluble, yielding a solution which has a green fluorescence, whereas the solutions of the salts of all the sulphonic acids hitherto referred to have a blue fluorescence. It can be converted into naphthalene-1 : 3 : 2'-trisulphonic acid, and since this can only yield two β-amido-derivatives, one of which has been described above, the constitution of this acid is proved.

*2-Naphthylamine-*1 : 3 : 3' : 2'*-tetrasulphonic acid* forms a characteristic *barium* salt, which is only very sparingly soluble in boiling water. When an acid solution of one of the salts of this acid is boiled, the sulphonic group in position 1 is removed in the form of sulphuric acid, whilst alkaline solutions may be evaporated without any decomposition occurring.

The formation of 2-naphthylamine-3 : 3' : 2'-trisulphonic acid is the first well established exception to the Armstrong-Wynne rule, and

the formation of the two isomeric, trisulphonic acids from napthyl-amine-1 : 3 : 2'-trisulphonic acid at 130° in the presence of sulphuric anhydride, is, moreover, a very important instance of molecular change among this class of compounds.

Sulphonation of 2-*Naphthol*-2'-*sulphonic acid.* When this acid is sulphonated by means of concentrated acid at 100° the 3 : 2'-disulphonic acid is formed without any isomeride, but accompanied by the 1 : 3 : 2'-trisulphonic acid. When chlorosulphonic acid is employed, however, the reaction proceeds differently, 2-*naphthol*-1 : 2'-*disulphonic acid* being formed in the cold. The *potassium* salt of this acid forms compact crystals, readily soluble in hot water. This acid does not yield azo-colouring matters, and can be converted into the corresponding naphthylamine compound, of known constitution, by heating with ammonia. When boiled with acids, the sulphonic group in the α-position is eliminated.

2-*Naphthol*-1 : 3 : 2'-*trisulphonic acid* is prepared by treating 2-naphthol-2'-sulphonic acid with fuming sulphuric acid at 80—90° for some hours. The *sodium* and *barium* salts are readily soluble and the acid does not yield azo-colouring matters. When boiled with acids, it is converted into the 3 : 2'-disulphonic acid.

2-*Naphthol*-1 : 3 : 3' : 2'-*tetrasulphonic acid* is the sole product formed by the further sulphonation of the foregoing acid at 130°. The *sodium* salt is readily soluble, the *barium* salt sparingly soluble in water. The acid does not yield azo-colouring matters, and when boiled with acids is converted into the 2 : 3 : 3'-*trisulphonic acid.* The latter forms a *sodium* salt which is characterised by its slight solubility in water. The acid readily yields azo-colouring matters and, when heated with ammonia, passes into the corresponding 2-naphthylamine-3 : 3' : 2'-trisulphonic acid which has been described above.

<div align="right">A. H.</div>

Crystalline Form of β-Methylnaphthalene. By H. WICHELHAUS (*Ber.,* **27**, 1247).—The preparation of this compound has been previously described (Abstr., 1892, 492). When gently heated, it sublimes and forms large lustrous monoclinic plates $a : b : c = 1·3040 : 1 : ?$ $β = 76° 44'$. The observed forms were OP and ∝P. There is complete cleavage parallel to the base.   J. B. T.

Dinitrochrysin. By G. DARIER (*Ber.,* **27**, 1045).—The nitro-chrysin obtained by Piccard and quoted by the author (this vol., i, 207) as mononitrochrysin, is actually the dinitro-compound, identical with that described by the author.   A. H.

The Crystalline Constituents of Coto Bark. By O. HESSE (*Ber.,* **27**, 1182—1186).—Re-examining his old specimens of cotoïn and cotoïn acetate, the author confirms the formulæ $C_{14}H_{12}O_4$ and $C_{14}H_{10}O_4Ac_2$, put forward by Ciamician and Silber (this vol., i, 255). He has also confirmed this molecular weight by Raoult's freezing-point method. The author believes that the methoxyhydroxyphenyl-coumarin acetate obtained by Ciamician and Silber when acetylising cotoïn was due to impurity of their material, as he obtained no such compound. Cotoïn appears to be dimorphous, crystallising in prisms and plates, both of which yield the same acetate.

The substance previously described by the author and Jobst as dicotoïn appears not to be a single substance. When acetylated, it yields cotoïn acetate. When fused with potash, it yields benzoic acid, the methoxyhydroxyphenylcoumarin of Ciamician and Silber (*loc. cit.*), and a substance to which the author ascribes the name oxymethyl-phenylcoumarin and the formula $O{<}{\begin{array}{c}C{\cdot}Ph{-\!\!-\!\!-}CO\\CH{\cdot}C_6H_3Me\end{array}}{>}O$. This substance crystallises in long, white needles, melts at 221°, and is soluble in alcohol. It does not yield an acetate with acetic anhydrides, neither does hydriodic acid eliminate methyl iodide. The compound, therefore, does not contain either a hydroxy- or methoxy-group. An analogous oxyphenylcoumarin melting at 61°, and giving no coloration with an alcoholic solution of ferric chloride, was also obtained from dicotoïn, by treating it with light petroleum.

How these compounds exist in the dicotoïn, whether free or combined, remains undetermined.   L. T. T.

The Pyridine Series. By W. MARCKWALD (*Ber.*, **27**, 1317—1339). —The formation of 2 : 5 amidonicotinic acid from the corresponding chloronicotinic acid and ammonia has already been described (Abstr., 1893, i, 727). Several derivatives of the amido acid, with both positive and negative radicles, are now described, among them the *picrate*, which melts at 248°.

2-Amidopyridine (*loc. cit.*) forms a *platinochloride*, melting at 231°, a picrate melting at 216—217°, and a *benzoyl* derivative, $C_5H_4{\cdot}NHBz$, melting at 165°; the latter yields a picrate melting at 146°. *Pyridyl-phenylthiocarbamide*, $C_5NH_4{\cdot}NH{\cdot}CS{\cdot}NHPh$, can only be obtained by boiling 2-amidopyridine with alcohol and phenylthiocarbimide; it forms white, lance-shaped crystals, and melts at 168°. 2-Amidopyridine remains unaltered when sodium nitrite is added to its solution in dilute hydrochloric acid; if, however, a strong solution of sodium nitrite is added to its solution in concentrated hydrochloric acid, 2-chloropyridine is formed. Nitrous acid does not react with 2 : 3-amidonicotinic acid in presence even of concentrated hydrochloric acid, but it is diazotised when its solution in concentrated sulphuric acid is treated with pulverised sodium nitrite in the cold.

Amidolutidinedicarboxylic acid, $N{<}{\begin{array}{c}CMe{\cdot}C(COOH)\\CMe{:}C(COOH)\end{array}}{>}C{\cdot}NH_2$, is obtained by treating chlorolutidinedicarboxylic acid (Conrad and Epstein, Abstr., 1887, 501) with ammonia at 130°; it crystallises from hot water in long, white needles, forms derivatives with both positive and negative radicles, and melts at 263° with evolution of carbonic anhydride, 4-*amidolutidine* being produced. The latter melts at 186°, and boils at 246°; the *picrate* melts at 194—195°, and the *platino-chloride* decomposes at 250°. The *acetyl*-derivative, $C_7NH_8{\cdot}NHAc$, crystallises from water in long, monohydrated needles melting at 78°; the *anhydrous* compound melts at 113°, forms a *platinochloride* melting at 235°, and a *picrate* melting at 97—98°. 4-Amidolutidine yields Conrad and Epstein's chlorolutidine (*loc. cit.*), when it is dissolved in concentrated hydrochloric acid and treated with sodium nitrite; when diazotised in presence of concentrated sulphuric acid, however, if the

resulting liquid be diluted by the addition of ice, lutidone sulphate is formed, whilst, if it be poured into absolute alcohol, *ethoxylutidine*, $N{<}{CMe{\cdot}CH \atop CMe{:}CH}{>}C{\cdot}OEt$, is obtained. This is a colourless, transparent liquid boiling at 207°; the *platinochloride* melts and decomposes at 204°, and the *picrate* melts at 112°. 4-Amidolutidine remains unaltered when treated with tin and hydrochloric acid, but may be reduced by sodium and alcohol, giving rise to 2 : 5 lupetidine (Ladenburg, *Annalen*, **247**, 87), the *thiocarbamate* of which melts at 108°, and *amidolupetidine*, $NH{<}{CHMe{\cdot}CH_2 \atop CHMe{\cdot}CH_2}{>}CH{\cdot}NH_2$, which boils at 195—196°. Ethoxylutidine yields lupetidine on reduction with sodium and alcohol. *Bromamidolutidine*, $N{<}{CMe{-}CH \atop CMe{:}CBr}{>}C{\cdot}NH_2$, is obtained by adding the calculated quantity of bromine to a solution of 4-amidolutidine in hydrochloric acid; it crystallises from water in monohydrated felted needles, melting at 89°; the *anhydrous* compound melts at 129°, and distils without decomposition. The *platinochloride* melts at 220°, and the *picrate* melts at 197—198°. *Dibromamidolutidine*, $N{<}{CMe{\cdot}CBr \atop CMe{:}CBr}{>}C{\cdot}NH_2$, forms white needles, melts at 152°, and can only be diazotised when dissolved in concentrated sulphuric acid, under which circumstances dibromolutidine is produced. *Dibromolutidine platinochloride* melts at 270°, and the *picrate* melts at 255°.

Nitramidonicotinic acid (Abstr., 1893, i, 727) is prepared by adding amidonicotinic acid nitrate to concentrated sulphuric acid, and gradually raising the temperature to 100°; when diazotised in presence of concentrated sulphuric acid, it yields *nitrohydroxynicotinic acid*,

$$N{<}{C(OH){\cdot}C(NO_2) \atop CH{=}C(COOH)}{>}CH \quad \text{or} \quad NH{<}{CO{-}\!-\!C(NO_2) \atop CH{:}C(COOH)}{>}CH,$$
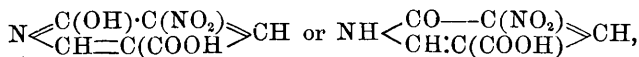
which forms feathery crystals, and melts with decomposition at 250°.

Diamidonicotinic acid, $N{<}{C(NH_2){\cdot}C(NH_2) \atop CH{=}C(COOH)}{>}CH$, is obtained by reducing the nitro-compound, preferably with tin and hydrochloric acid; it forms a grey powder containing $1H_2O$, which is expelled at 120°, and does not melt at 300°; its basic properties are more pronounced than its acidic; the *picrate* melts at 245°.

Azimidonicotinic acid, $COOH{\cdot}C{<}{CH{-}\!-\!C{-}N \atop CH{\cdot}N{\cdot}C{\cdot}NH}{>}N$, is obtained by treating the last-mentioned diamido-derivative with nitrous acid; it separates from water in white, felted crystals, containing $1H_2O$, and decomposes at about 270°.   A. R. L.

3-Chloroquinoline. By A. CLAUS and A. SCHEDLER (*J. pr. Chem.*, [2], **49**, 355—378).—3-Chloroquinoline melts at 40—41°, and boils at 261—262° (740 mm.). The *perbromide* of its hydrobromide, $C_9NH\,Cl,HBr,Br_2$, crystallises in yellow needles, and melts and decomposes at 129°. When heated at 180—190°, the perbromide yields the hydrobromide of 4'-*bromo*-4-*chloroquinoline*; the free base crystal-

lises in small, colourless needles, melts at 112°, and is volatile with steam; the *hydrochloride* (m. p. 168°), *platinochloride* and *methiodide* (m. p. 286—287°) are described.

4-*Nitro-3-chloroquinoline* crystallises in colourless prisms, melts at 129°, and sublimes when heated; the *hydrochloride* melts and decomposes at 215°; the *platinochloride* does not melt at 320°; the *nitrate* melts and decomposes at 194°; the *methiodide* melts at 243°. The *methochloride* melts and decomposes at 178°; its *platinochloride* is described. The *sulphate* melts at 227—228°.

4-*Amido-3-chloroquinoline* crystallises (with $1H_2O$) in long, silky, yellow needles; the crystals melt at 115—119°, and the anhydrous compound melts at 132—136°. The *hydrochloride* crystallises in blood-red tables, melts at 215—220°, and dissolves in water and alcohol; the *platinochloride* melts and decomposes at 250°.

4 : 3-*Dichloroquinoline*, prepared from the amido-derivative through the diazo reaction, crystallises in colourless needles, melts at 85°, and dissolves in alcohol and in light petroleum, but only sparingly in hot water; the *platinochloride* is described.

4-*Hydroxy-3-chloroquinoline* is obtained when the 4-diazo-3-chloro-quinoline sulphate is treated with dilute cuprous chloride solution; it crystallises in vitreous needles, melts at 183—184°, and dissolves in most solvents; the *platinochloride* and the *methiodide* (m. p. 199—201°) were obtained.

1-*Nitro-3-chloroquinoline* is a bye-product in the nitration of quinoline in sulphuric acid, but the sole product when nitric acid is used alone; it crystallises in slender, colourless needles, melts at 158°, sublimes, and dissolves in alcohol and in hot water; the latter solvent separates it from the 4-nitro-derivative. The *platinochloride* decomposes at 251°.

1-*Amido-3-chloroquinoline* crystallises in colourless needles, melts at 73°, and sublimes. It forms two *hydrochlorides*; $NH_2 \cdot C_9NH_5Cl, 2HCl$ forms large, red crystals, melts at 228°, and is decomposed by water into $NH_2 \cdot C_9NH_5Cl, HCl$, which forms small, yellow crystals, and melts at 208°. The *platinochloride* of the latter salt is described. The methiodide of this amidochloroquinoline crystallises in orange-yellow needles, and melts at 178°.

3-*Chloroquinoline-4-sulphonic acid* crystallises, with $1H_2O$, in tables; its *potassium* salt, with $1\frac{1}{2}H_2O$, is described.

3-*Chloroquinoline-1-sulphonic acid* crystallises in colourless, vitreous needles; its *potassium* salt is described.　　　　　　　　　　A. G. B.

Reduction and Condensation of Thiazoles. By A. SCHUFTAN (*Ber.*, **27**, 1009—1012).—According to Schatzmann (*Annalen*, **261**, 6), dimethylthiazole is converted, by reduction with sodium and alcohol, into ethylamine and propyl mercaptan. When, however, the reduction is effected by adding the heated solution of the thiazole in alcohol to the sodium, *ethylisopropylamine*, $NHEtPr^\beta$, and hydrogen sulphide are formed. The new base is a colourless liquid, which is miscible with water and alcohol, and boils at 76°. The *platinochloride* crystallises in reddish-yellow needles melting at 180°. Nitrous acid converts the base into *ethylisopropylnitrosamine*, which is a

yellow oil boiling at 70° (11 mm.). *Ethylisopropylphenylthiocarb-amide*, $NEtPr^\beta \cdot SC \cdot NHPh$, forms long, white, very refractive needles, and melts at 132°.

When dimethylthiazole is heated at 160° with formaldehyde solution, *dimethylthiazolylalkine*, $\overset{S-CH}{\underset{CMe:N}{|}}{>}C \cdot CH_2 \cdot CH_2 \cdot OH$, is formed. This compound is an oily, faintly alkaline liquid. The *platinochloride* melts and decomposes at 169°; the *hydrochloride* crystallises in fan-shaped groups of long, colourless needles, and the *aurochloride* melts at 136°. A. H.

Pyrazines. By C. Stoehr (*J. pr. Chem.*, [2], **49**, 392—403).—This paper constitutes a rejoinder to Wolff (Abstr., 1893, i, 729).

Methylpyrazine, $C_4H_3MeN_2$, is a limpid, strongly refractive, colourless liquid; it remains liquid at 0°, boils at 136—137°, and has a specific gravity of 1·0441 at 0°/4°.

Pyrazine picrate melts at 156°. Pyrazine methiodide crystallises in yellow laminæ, and is insoluble in ether and benzene, but soluble in alcohol. A. G. B.

Constitution of Phenylpyrazolone. By S. Ruhemann and R. S. Morrell (*Ber.*, **27**, 1090—1091).—In connection with the recent work of Stolz (this vol., i, 259) and v. Rothenburg (this vol., i, 350), the authors show that the phenylpyrazolone melting at 118° prepared by them (Trans., 1892, 791) can only be 1-phenyl- 3 or 5-pyrazolone. W. J. P.

Cyanacetophenone and Hydroxylamine. By R. v. Rothenburg (*Ber.*, **27**, 1095—1096).—The compound obtained by the interaction of these substances, and described by Obregia (Abstr., 1892, 324), has not the properties of a pyrazolone derivative. It is, therefore, not 3-phenylpyrazolone, as Obregia supposed, but is probably 3-phenyl-5-imido-oxazoline, $\overset{CPh \cdot CH_2}{\underset{N-----O}{||}}{>}C{:}NH$, or else the tautomeric 3-phenyl-5-amido-oxazole, $\overset{CPh \cdot CH}{\underset{N----O}{||}}{>}C \cdot NH_2$. C. F. B.

3 : 5-Dimethylpyrazole. By R. v. Rothenburg (*Ber.*, **27**, 1097—1098; compare Marchetti, Abstr., 1893, i, 179 and 674, and Buchner and Papendieck, *ibid.*, 432).—Hydrazine hydrate and ethyl-acetone yield 3 : 5-*dimethylpyrazole*, $\overset{N{=\!=}CMe}{\underset{NH \cdot CMe}{|}}{>}CH$, which melts at 105—108°, and boils at about 220°; its *platinochloride*,

$$(C_5H_8N_2)_2, H_2PtCl_6 + 2H_2O,$$
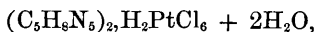
decomposes at about 180°. When oxidised with the theoretical amount of alkaline permanganate, it yields Marchetti's 5-methylpyrazole-3-carboxylic acid, $\overset{N{:}C(COOH)}{\underset{NH----CMe}{|}}{>}CH$. If double the above

quantity of permanganate is used. 3 : 5-pyrazoledicarboxylic acid is formed, already described by Marchetti and by Buchner.

C. F. B.

Pyrazolone from β-Aldoximeacetic acid. By R. v. ROTHEN-BURG (*Ber.*, **27**, 1098—1099).—Pechmann's β-aldoximeacetic acid (β-oximidopropionic acid), $NOH:CH\cdot CH_2\cdot COOH$ (Abstr., 1891, 1458), was first prepared in solution by warming together coumalinic acid, hydroxylamine hydrochloride, and soda ; and to the mixture, neutralised with hydrochloric acid, the calculated quantity of hydrazine hydrate was added, and the whole allowed to remain at 50—60°. The hydroxylamine salt of the pyrazolone thus formed can be separated into its constituents by adding sodium carbonate, and distilling over the pyrazolone with steam.

C. F. B.

Isomeric n-Phenylpyrazolones. By R. v. ROTHENBURG (*Ber.*, **27**, 1099—1100).—The compound erroneously described (*Ber.*, **27**, 946) as 2-phenylisopyrazolone-3-carboxylic acid is really 2-phenyliso-pyrazolone-4-carboxylic acid, $\begin{smallmatrix} NPh\cdot CH \\ | \\ NH—CO \end{smallmatrix}\!\!>\!\!C\cdot COOH$.

C. F. B.

Octohydro-1 : 8-naphthyridine and 2ω-Amidopropylpiperid-one. By A. REISSERT (*Ber.*, **27**, 979—984 ; compare Abstr., 1893, i, 687).—When di-γ-amidodipropylacetic acid, containing a certain amount of carbonate, formed by absorption of atmospheric carbonic anhydride, is submitted to dry distillation, octohydronaphthyridine passes over, whilst a residue consisting of the carbonate of *2ω-amido-propylpiperidone*, $CH_2\!\!<\!\!\begin{smallmatrix} CH_2\cdot CH_2 \\ | \\ NH—CO \end{smallmatrix}\!\!>\!\!CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2$, is left. By the action of strong soda on this salt, the free base is obtained as a colourless, odourless, strongly basic oil, which is tolerably soluble in water ; it gives the carbylamine reaction, and cannot be distilled, since, when heated, it decomposes into water and octohydronaphthyridine. The *hydrochloride*, $C_8H_{16}N_2O,HCl$, melts at 159·5°, and the *platinochloride* at 220°. The *picrate* forms soft, yellow needles melting at 207°. Benzoic chloride converts the base into a *monobenzoyl derivative*, $C_8H_{15}N_2O\cdot COPh$, which melts at 151°.

Octohydronaphthyridine, $\begin{smallmatrix} CH_2\cdot CH_2\cdot CH\cdot CH_2\cdot CH_2 \\ | \qquad\qquad | \\ CH_2—N:C\cdot NH—CH_2 \end{smallmatrix}$, forms white needles, melts at about 67°, and boils at 248°. It combines very readily with the atmospheric carbonic anhydride, forming the *carbonate*, which is readily soluble in water, and melts at 156°. The free base is readily soluble in water, and moderately so in alcohol, forming strongly alkaline solutions ; it has a characteristic alkaloïdal odour. The *hydrochloride* could only be obtained as a syrup ; the *picrate* melts at 208—209°.

n-*Methyloctohydronaphthyridine* is prepared by the direct action of methylic iodide on the base or its carbonate. It is a basic oil, and yields a *picrate*, which melts at 209°.

A. H.

Action of Hydrazine on Imido-Ethers. By A. PINNER (*Ber.*, **27**, 984—1009 ; compare Abstr., 1893, i, 710).—When benzimido-

ether and hydrazine are brought together, *benzenylhydrazidine*, $NH_2 \cdot NH \cdot CPh \colon NH$, is the first product, and this immediately reacts with hydrazine or benzimido-ether to produce secondary compounds. The free base cannot be obtained pure, but the *picrate*,

$$C_7H_9N_3, C_6H_3N_3O_7,$$
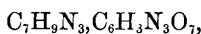
may be prepared by treating benzimido-ether hydrochloride with hydrazine sulphate dissolved in aqueous potash, filtering off the dibenzenylhydrazidine which separates, acidifying, and, after some days, adding picric acid. It forms short, thick, yellow prisms, and is soluble in alcohol and hot water.

Benzoylbenzenylhydrazidine, $COPh \cdot NH \cdot NH \cdot CPh \colon NH$, may be obtained by shaking the alkaline filtrate mentioned above with benzoic chloride. It crystallises in long, lustrous prisms, and melts, after losing the elements of water, at 188°. This substance is identical with the compound formerly described (*loc. cit.*) as melting at 170°. It is a strong base and reduces copper solution on boiling. The *aurochloride* crystallises in yellow prisms and melts at 197°. When it is heated to 120°, it is converted into diphenyltriazole.

Benzenylhydrazidine is converted by the action of nitrous acid into phenyltetrazotic acid, identical with that described by Lossen (*Annalen*, **263**, 101). It also reacts with glyoxal to form *glyoxalenedibenzenylhydrazidine*, $C_2H_2(N \cdot NH \cdot CPh \colon NH)_2$, which crystallises in short, slender, lustrous, yellow needles, is only slightly soluble in the usual solvents, and melts and decomposes at 220°, after softening at 210°.

Dibenzenylhydrazidine, $N_2H_2(CPh \colon NH)_2$, has been previously described. It appears in many reactions to behave as a diamido-compound of the formula $NH_2 \cdot CPh \colon N \cdot N \colon CPh \cdot NH_2$. It is a strong diacid base, and is very unstable in acid solution although stable in alkaline liquids. The hydrochloride, $C_{14}H_{14}N_4, 2HCl$, sublimes, when heated, without melting. The *nitrate* forms white, sparingly soluble prisms, and melts at 114°, whilst the *picrate* melts at about 220°. *Diacetyldibenzenylhydrazidine* forms white needles melting at 98°, and is readily soluble in alcohol.

When dibenzenylhydrazidine is allowed to remain in acid solution for some time, or when it is treated with zinc dust and acetic acid, it is converted into *diphenyltriazole*, $CPh{<}^{N —}_{NH \cdot N}{>}CPh$; this crystallises with $1H_2O$ in white prisms which effloresce at 100° ; it is insoluble in water and in dilute acids, moderately soluble in alcohol, melts at 188°, and boils and decomposes at about 280°. *Acetyldiphenyltriazole* melts at 105°.

The action of nitrous acid on dibenzenylhydrazidine is of a complex character, and varies with the conditions of the experiment. When a large excess of sodium nitrite and acetic acid is used, phenyltetrazotic acid and dibenzamide are the main products, the latter being probably formed from benzonitrile, the primary reaction being as follows: $C_{14}H_4N_4 + HNO_2 = C_7H_6N_4 + C_7H_5N + 2H_2O$. When 2 mols. of sodium nitrite and hydrochloric acid are employed, a crystalline precipitate is formed, consisting of the *hydrochloride of benzoyl-*

benzenylhydrazidine, $C_{11}H_{13}N_3O,2HCl$, which melts at 92°, solidifies when further heated, and finally melts at 172°. It is remarkable that benzenylhydrazidine is a monacid base, whilst the benzoyl-derivative combines with 2 molecules of an acid. In this reaction, dibenzenylhydrazidine reacts as though it contained two amido-groups.

When 4 mols. of sodium nitrite are used, and the mixture is allowed to remain over night, a mass of white crystals is obtained. These are readily soluble in alcohol, slightly in benzene, and melt and deflagrate at 110°. The compound shows Liebermann's reaction, and has the formula $OH·CPh:N·N:CPh·NH·NO,HCl + H_2O$. When it is heated with water, benzoylbenzenylhydrazine is formed.

If the same mixture, containing 4 mols. of sodium nitrite, be allowed to remain for 4—8 days, the crystalline mass partially dissolves, benzoylbenzenylhydrazidine and dibenzenylisazoxime, $CPh \lll_{N·N}^{-O-} \ggg CPh$, being formed. In all these reactions, a small amount of phenyltetrazotic acid is also produced.

Diphenyldihydrotetrazine, $CPh \lll_{N——N}^{NH·NH} \ggg CPh$, is the chief product of the action between 2 mols. of benzimido-ether and 3 mols. of hydrazine sulphate. It does not appear to be formed from dibenzenylhydrazidine by the action of hydrazine, and is probably, therefore, derived from the monobenzenylhydrazidine in the presence of hydrazine. It unites with methylic iodide to form the *double compound*, $C_{14}H_{12}N_4,MeI$, which melts and decomposes at 128°.

When diphenyldihydrotetrazine is heated with acetic acid and zinc dust, or alcohol and sodium, diphenyltriazole is formed ; if, on the other hand, it is boiled with hydrochloric acid of 25 per cent., it is converted into the isomeric *diphenylisodihydrotetrazine*, $CPh \lll_{NH·N}^{N·NH} \ggg CPh$. This compound was described in the previous paper under the name of benzenylimidonitrile as having half the molecular weight which is now ascribed to it. The *aurochloride* melts at 215°. *Monacetyldiphenylisodihydrotetrazine* melts at 267° and forms small white prisms. The *diacetyl*-derivative forms compact, white prisms, which melt at 215°. The diacetyl-derivative obtained from diphenyldihydrotetrazine was found to have the constitution which had previously been ascribed to it.

Diphenylisodihydrotetrazine is converted by nitrous acid into diphenyltriazole ; like its isomeride, this combines with 1 mol. of methylic iodide to form a substance, which crystallises in compact prisms and melts and decomposes at 150°. *Dibenzenylisazoxime* or *diphenylbiazoxole*, $CPh \lll_{N·N}^{-O-} \ggg CPh$, has already been mentioned as being formed by the action of nitrous acid on benzoylbenzenylhydrazidine and dibenzenylhydrazidine. From hot alcohol, to which a little potash has been added, it crystallises in large iridescent plates of the anhydrous substance, whilst, by the evaporation of the cold solution, slender needles are obtained, which contain $1H_2O$. The hydrated crystals melt at 80°, the anhydrous at 140°, and the compound distils, without decomposing, above 360°. The isazoxime combines with

silver nitrate to form long, silky needles, which are acted on by light and melt and decompose at 275°.

Although diphenyldihydrotetrazine is scarcely affected by aqueous soda, its oxidation product, diphenyltetrazine, is converted by the action of alcoholic potash into a compound of the constitution CHPh:N·N:CPh·OH, which crystallises in lustrous, colourless prisms, melts at 206°, and is slightly soluble in alkalis, insoluble in acids.

Dibenzimidine, $C_{14}H_{13}N_3$, which is also found among the products of the reaction between benzimido-ether and hydrazine, is probably formed from the benzenylhydrazidine. It yields a *triacetyl*-derivative, which melts at 94°, and an *aurochloride*, which melts at 145°. It is soluble in concentrated hydrochloric acid and in strong aqueous alkalis.   A. H.

Coniine and its Compounds. By J. SCHORM (*Zeit. angw. Chem*, 1894, 266—267).—In extracting coniine from hemlock seeds, the author recommends, as an improvement on his previously described method (Abstr., 1882, 215), that the crude solution of chlorides should be evaporated to dryness and the residue heated on the sand bath until the resinous impurities are destroyed and the residue has become odourless. It is then dissolved and filtered, and if the filtrate is coloured, should be treated with animal charcoal, or, better, with hydrogen peroxide, until colourless, and the solution evaporated to a small bulk; coniine hydrobromide crystallises out whilst the mother liquor contains conhydrine and a new base. To obtain these, the solution is rendered alkaline and the bases extracted with ether, from which extract the conhydrine crystallises out, leaving the new base (which is under investigation) as an oil.

The hydrated coniine (in the form in which it separates from the steam distillate) has a sp. gr. of 0·900 at 12°, and at 100° gives up 20 per cent. of water, passing into the anhydrous base. It is the best form in which to keep the base. The author has prepared many of the salts from the pure base.

The author recommends the use of hydrogen peroxide for purifying natural alkaloïds, but it must only be used in neutral solutions of the chlorides, or it is liable to cause loss of the alkaloïd.

                                                        L. T. T.

Nicotine (Metanicotine). By A. PINNER (*Ber.*, **27**, 1053—1061). —The substance prepared by Étard (Abstr., 1893, i, 736) and considered by him to be benzoylnicotine, is really a benzoyl-derivative of a secondary base isomeric with nicotine, which the author terms metanicotine. The derivative is hence benzoylmetanicotine.

Benzoylmetanicotine picrate, $C_{10}H_{13}N_2 \cdot OBz, \ddot{C}_6H_3N_3O_7$, crystallises in thin, flattened prisms melting at 128°, and is soluble in alcohol; it is advantageously employed in place of the platinochloride in the purification of the base.

Metanicotine, $C_{10}H_{14}N_2$, is prepared by heating its benzoyl-derivative with concentrated hydrochloric acid in a closed tube at 100°; it boils at 275—278°, has a feeble odour recalling that of nicotine, is optically inactive, and has more pronounced basic properties than nicotine. It

is sparingly soluble in ether. A benzoyl-derivative, identical with that prepared from nicotine, is obtained on adding benzoic chloride to its solution in soda. The *hydrochloride*, $C_{10}H_{14}N_2,2HCl$, forms a colourless, hygroscopic, crystalline mass, and is readily soluble in water or alcohol. The *platinochloride* crystallises in beautiful, yellow prisms, decomposing with partial fusion at about 255°. The *aurochloride* forms yellow prisms melting at 160° on rapid heating, whilst *nicotine aurochloride* is obtained as a scarcely crystalline precipitate, decomposing with partial fusion at above 180°. *Metanicotine picrate*, $C_{10}H_{14}N_2,2C_6H_3N_3O_7,H_2O$, is obtained in thin, crystalline threads, melting first at 114°, then solidifying and again melting at 163°.

The author again (Abstr., 1893, i, 736) criticises adversely the constitutional formula attributed by Etard to nicotine ; the base is probably a methyl-β-pyridylpyrrolidine, having the constitution

$$\begin{matrix} CH\text{:}CH\cdot CHNMe\cdot CH_2 \\ | \quad || \quad | \\ N\text{=}CH\cdot C-CH-CH_2 \end{matrix}\!\!\!>\!\!CH_2\ ;$$
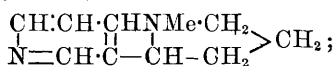
metanicotine would then probably be methyl-β-pyridyl-δ-butylen-amine, $CH\!\!<\!\!\begin{matrix}CH\cdot CH \\ N\text{=}CH\end{matrix}\!\!>\!\!C\cdot CH\text{:}CH\cdot CH_2\cdot CH_2\cdot NHMe.$ W. J. P.

Hydrastine. By E. SCHMIDT (*Arch. Pharm.*, **231**, 541—579; compare Abstr., 1890, 533, 1168; 1893, i, 116).—The author describes the decomposition of hydrastonic acid, and strengthens the evidence in favour of the constitutional formula for hydrastine advocated by Freund (*Annalen*, **271**, 345), supporting his conclusions by a further study of the methyl derivatives of the alkaloïd.

Hydrastonic acid is the non-nitrogenous substance melting at 169°, obtained by decomposing methylhydrastine methiodide with aqueous potash (Abstr., 1890, 533 and 1168). Analysis of the free acid and of its silver salt establishes its monobasic character, and confirms the composition, $C_{20}H_{18}O_7$, already ascribed to it. Hydrastonic acid contains two methoxyl groups, and, whilst not attacked by acetic chloride, unites readily with hydroxylamine to form an *oxime*, $C_{20}H_{18}O_6$:NOH ; the addition of 2 atoms of bromine affords evidence of the unsaturated character of the acid. Oxidation in neutral solution with potassium permanganate gives rise to hemipinic acid, together with an acid of unknown constitution, which melts at 234°. If, however, an alkaline solution is employed, *hydrastolactone*, $C_{10}H_8O_5$, is formed ; this crystallises in long needles, and melts at 154°. It resembles in its properties cotarnelactone (Abstr., 1890, 528), the intermediate product in the oxidation of cotarnone to cotarnic acid. The *benzoyl*- and *acetyl*-derivatives are well defined, the latter forming thick rectangular plates which melt at 115°. In addition to hydrastolactone, the oxidation of hydrastonic acid leads to the formation of hemipinic, hydrastic, and oxalic acids, together with a small quantity of an unknown monobasic acid, isomeric with hemipinic acid, but differing from it in character, for whilst the latter substance melts at 162° the new acid fuses with evolution of gas at 146—148°, resolidifies at 167°, and finally melts at 220°. The resemblance shown by hydrastolactone to cotarnelactone is borne out by its behaviour on further

oxidation with potassium permanganate, this treatment giving rise to hydrastic acid (Abstr., 1893, 117).

The relative position of the oxymethylene and the two carboxyl groups in hydrastic acid is shown by reducing it with phosphorus and hydrogen iodide, normetahemipinic acid, $C_8H_6O_6$, being formed; hydrastic acid, therefore, has the constitution

$$CH_2 \overset{5}{\underset{4}{\overset{O}{\underset{O}{<}}}} \!\! > C_6H_2(\overset{1:2}{COOH})_2,$$
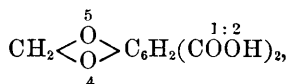
hydrastolactone, from which it is derived by oxidation, being represented by the formula $CH_2 \!\! <^O_O \!\! > \!\! C_6H_2 \!\! <^{CO \underline{}}_{CH(CH_2 \cdot OH)} \!\! > \!\! O$. Since this lactone and hemipinic acid are the principal products of the oxidation of hydrastonic acid, the latter must have the constitution
$\overset{4.5}{CH_2} \!\! : \!\! O_2 \!\! : \!\! C_6H_2(\overset{2}{CH} \!\! : \!\! CH_2) \cdot \overset{1}{CH_2} \cdot \overset{4}{CO} \cdot C_6H_2(\overset{1:2}{OMe})_2 \cdot \overset{3}{COOH}$, this being in agreement with its ketonic, acid, and unsaturated character, the molecule, on oxidation, breaking down between the carbonyl and methylene groups.

Before drawing a final conclusion as to the constitution of hydrastine, it was desirable to study the behaviour of methylhydrastine, methylhydrastine hydroxide (Abstr., 1890, 1168), and the alkaloïd itself, towards hydroxylamine. It is found that hydrastine does not contain a carbonyl group, but the two first-named compounds yield a derivative of the composition $C_{22}H_{24}N_2O_6$, crystallising in plates which melt at 158—159°. This substance is not acetylated by acetic anhydride or chloride, but under the influence of these reagents takes up 1 H_2O, being converted into the oxime of methylhydrastine hydroxide, $C_{22}H_{26}N_2O_7$, which forms transparent prisms melting at 202—203°. This oxime is feebly acid in character, but hydrogen chloride regenerates the hydrochloride of the compound $C_{22}H_{24}N_2O_6$, which must be regarded as the anhydride of the oxime of methylhydrastine hydroxide.

From a consideration of these facts, the author is led to regard hydrastine as having the constitution

$$\overset{4,5}{CH_2} \!\! : \!\! O_2 \!\! : \!\! \underset{2}{C_6H_2} \!\! \underline{} \overset{1}{CH} \cdot \overset{4}{CH} \cdot C_6H_2(\overset{1,2}{OMe})_2$$
$$\overset{|}{CH_2} \cdot CH_2 \cdot \underset{|}{NMeO} \!\! - \!\! \underset{3}{CO}$$
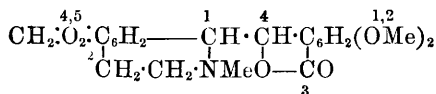
(compare Freund and Rosenberg, Abstr., 1890, 534).

Acetohydrastine, $C_{21}H_{20}AcNO_6$, is the product of the action of acetic chloride on hydrastine (Abstr., 1890, 649). It crystallises from alcohol in lustrous, yellowish-green needles melting at 202°, a solution in chloroform or alcohol exhibiting a strong fluorescence of the same shade. In this respect it resembles methylhydrastine, and, like this compound, unites with 2 atoms of bromine. The constitution of acetohydrastine is best represented by the formula

$$CH_2 \!\! : \!\! O_2 \!\! : \!\! C_6H_2(CH_2 \cdot CH_2 \cdot NMeAc) \cdot CH \!\! : \!\! C \!\! <^{O \cdot CO}_{- \, C_6H_2(OMe)_2}.$$
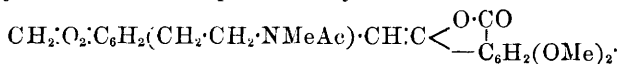
By boiling an alcoholic solution of hydrastine methiodide with a large excess of strong aqueous ammonia, methylhydrastamide has been obtained (Abstr., 1891, 92). If, however, the dry methiodide is heated for two hours with alcoholic ammonia at 100° under pressure, it yields *methylhydrastimide hydriodide*, $C_{22}H_{24}N_2O$,,HI, which crystallises from alcohol in yellow needles melting at 233°.

Hydrastinine, the product of the oxidation of hydrastine with dilute nitric acid (Abstr., 1887, 383), is obtained in small quantities when a mixture of hydrastine with 10 parts of soda-lime is submitted to dry distillation in an atmosphere of hydrogen.   M. O. F.

New Compounds of Cinchona Alkaloïds with Ethylic Iodide. By Z. H. SKRAUP and F. K. v. NORWALL (*Montash.*, **15**, 37—52).—In this paper, particulars are given of work which has been previously published in outline (compare Abstr., 1893, i, 738). In order to distinguish between the isomeric compounds of an alkaloïd with ethylic iodide, the authors suggest that one compound should be represented by the name of the alkaloïd preceded by the term " iodoethyl," whilst the second should be represented by a name in which that of the alkaloïd is followed by the term " ethiodide." For example, they propose to call the colourless product obtained from tree cinchonine and ethylic iodide, " iodoethylcinchonine," whilst the yellow substance prepared from cinchonine hydriodide and ethylic iodide would be named " cinchonine ethiodide."

The following compounds are described :—*Cinchonine ethiodide hydriodide*, $EtI,C_{19}H_{22}N_2O$,HI, crystallises in yellow prisms, commences to decompose, with evolution of iodine, at 200°, melts with decomposition at 245—250°, and when treated with ammonia yields *cinchonine ethiodide*. The latter crystallises from water in orange-yellow needles, blackens at 170°, and slowly melts at about 184°. *Iodoethylcinchonine hydriodide*, the isomeride, crystallises in pale yellow prisms, having the composition $EtI.C_{19}H_{22}N_2O$,HI + H_2O, melts at 220—222°, and is formed when a solution of iodoethylcinchonine (m. p. 259—260°) in hydrochloric acid is treated with potassium iodide. *Cinchonidine ethiodide hydriodide*, which crystallises in yellow prisms and melts at 243°, yields, when treated with ammonia, *cinchonidine ethiodide*, which forms small, yellow needles, and melts with decomposition at 175°. *Iodoethylcinchonidine hydriodide*, $EtI,C_{19}H_{22}N_2O$, + H_2O, crystallises in light yellow needles, is orange-yellow at 100—130°, loses iodine at 140—150°, and melts with decomposition at 231°.

Quinine ethiodide hydriodide, $HI,C_{20}H_{24}N_2O_2,EtI$ + $3H_2O$, crystallises from water in brownish-yellow scales, which melt at 75—80°, and from alcohol in deep yellow crystals, melting at 234°. Treated with sodium hydroxide or with ammonia, it forms *quinine ethiodide*, $C_{20}H_{24}N_2O_2,EtI$ + $3H_2O$. This crystallises from alcohol in long needles, softens at 85°, melts at 93°, and unites with ethylic iodide to form *quinine diethiodide* (m. p. 140°). *Iodoethylquinine hydriodide* melts at 200°, and crystallises in needles or small grains.

Quinidine diethiodide, $C_{20}H_{24}N_2O_2,2EtI$ + $3H_2O$, prepared from

colourless iodoethylquinidine and ethylic iodide at 100°, crystallises in bright yellow prisms and melts at 134°.   G. T. M.

The Hydrolytic Decomposition of Chinine and Cinchine.

By W. KOENIGS (*Ber.*, **27**, 900—907).—It has been shown that chinine and cinchine, when boiled with concentrated hydrogen bromide, are converted into derivatives of γ-phenylquinoline, namely, apochinine and apocinchine. If, however, cinchine and chinine are heated with phosphoric acid at 170—180°, they are decomposed, yielding lepidine and paramethoxylepidine respectively, and also a new compound, $C_9H_{15}NO_2$, which the author names merochinine.

For reasons which are given below, the author assigns the following constitutions to apocinchine and apochinine, namely,

$$\text{Apocinchine, } C_9NH_6 \cdot \overset{4'\ 1}{C_6}H_2\overset{3,\ 4\ 2}{Et_2} \cdot OH \text{ ; and}$$

$$\text{Apochinine, } \overset{3}{OH} \cdot C_9NH_5 \cdot \overset{4'\ 1}{C_6}H_2\overset{3,\ 4\ 2}{Et_2} \cdot OH.$$
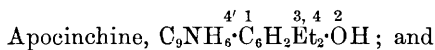
The author has already shown (Abstr., 1893, i, 376) that the ethyl ether of apocinchine, on oxidation, yields ethylapocinchenic acid, a lactone, and finally quinolinephenetoïldicarboxylic acid containing the two carboxyl groups in the ortho-position relatively to one another. The orthohydroxy-γ-phenylquinoline, prepared from orthomethoxy-benzoylacetone, is found to be identical with the hydroxyphenyl-quinoline obtained from apocinchine.

Apocinchine, when treated with sodium nitrite in acetic acid solution, yields a *mononitro-derivative*, melting at 228°, and this, on reduction, is converted into *amido-apocinchine*, melting at 220°. The latter, on oxidation, yields cinchoninic acid, and when dissolved in sulphuric acid and treated with lead peroxide, gives a dark red coloration, which is probably due to the formation of a quinone or quinhydrone.

When apochinine is heated with zinc chloride, ammonia, and ammonium chloride at 240—250°, it is converted into 4-amidoapocinchine, which melts at 226—228°, and this is converted through the diazo-compound into apocinchine.

Merochinine, $C_9H_{15}NO_2$, crystallises in colourless needles, melts at 222°, and cannot be distilled without decomposition. It is very similar to the cincholeupone obtained by Skraup (Abstr., 1889, 282, 626). When heated with concentrated hydrogen bromide, it gives carbonic anhydride, a large quantity of resin, and an oily base which boils at 170—177°. It is easily converted into its alkyl ethers, which yield well-characterised hydrochlorides. The *nitroso-compound* does not give Liebermann's reaction, and evolves red fumes when boiled with hydrobromic acid. When treated with bromine water, a compound $C_9NH_{14}BrO_2,HBr$, is obtained, which is very similar to the compound obtained by Skraup from cincholeupone.   E. C. R.

Organic Chemistry.

Stereoisomerism. By A. CLAUS (*J. pr. Chem.*, [2], **49**, 445—465). —A criticism of stereochemical theories, referring particularly to the recent exposition of the subject by V. Meyer (*Chem. Zeit.*, **17**, 1869).

<div align="right">A. G. B.</div>

Action of Chlorine on Methane in Natural Gas. By F. C. PHILLIPS (*Amer. Chem. J.*, **16**, 361—365).—The gas consisted of methane (95·4 per cent.), carbonic anhydride (0·2 per cent.), nitrogen (4·4 per cent.), and a trace of oxygen. When a mixture of the gas with chlorine was passed over red-hot lampblack, methylic chloride and carbon tetrachloride were formed in abundance, whatever the proportions. Methylene chloride and chloroform were found only in small quantities. The methylic chloride resembled that prepared from methylic alcohol in all respects except one, that it failed to form a crystalline hydrate with ice-cold water. This confirms v. Baeyer's results (*Annalen*, **107**, 269). The author does not agree with Roscoe and Schorlemmer's view (*Chemistry*, [3], **1**, 203), that this is due to the presence of higher chlorides, as especial pains were taken to remove the latter.

<div align="right">JN. W.</div>

Isomerides of Propylene and their Sulphates. By BERTHELOT (*Compt. rend.*, **118**, 1009—1013).—Propylene and trimethylene are both absorbed immediately by concentrated sulphuric acid at the ordinary temperature. A known weight of sulphuric acid was introduced into an eprouvette above some mercury, the latter acting as a conductor of heat, and thus preventing a rise of temperature. The dry gaseous hydrocarbon was gradually introduced into the vessel, and was absorbed at first rapidly and afterwards more slowly.

Trimethylene yields the normal sulphate $(C_3H_7)_2SO_4$, which, on addition of water, separates as a heavy neutral oil, only very slightly soluble in water. The salt undergoes very little decomposition, even if left in contact with water for several weeks.

Trimethylene sulphate distils in water vapour, but, when heated alone, it decomposes into sulphurous anhydride, volatile liquids, and a carbonaceous residue. Potassium hydroxide decomposes it after heating for several hours in a sealed tube at 100°, sulphuric acid and propylic alcohol being formed.

The author points out that pure ethylene, unlike trimethylene, is very slowly absorbed by sulphuric acid.

Propylene under similar conditions is rapidly absorbed by sulphuric acid, and yields the sulphate, $(C_3H_7)_2SO_4$, which resembles trimethylene sulphate in general physical properties, but is much less stable, and is dissolved and decomposed even by cold water in a few hours.

Isobutylene likewise yields a sulphate, $(C_4H_9)_2SO_4$, which is gradually decomposed by water.

<div align="right">C. H. B.</div>

Production of Cyanides. By H. N. WARREN (*Chem. News*, **69,**
186—187).—Attention is drawn to the small amounts of cyanide pro-
duced by igniting potassium nitrate with Rochelle salt or sodium
acetate, or even when the nitrate is made into briquettes with wheat
flour and magnesia and ignited; to the occasional inferiority of the
product from thiocyanates; and to the value of the addition of lime
or baryta when preparing cyanides by the incineration of nitrogenous
compounds.   D. A. L.

**Combination of Molybdenum Dioxide and Bisulphide with
Alkali Cyanides.** By. E. PÉCHARD (*Compt. rend.*, 118, 804—807).—
See this vol., ii, 319.

Ethylallylcarbinol. By H. FOURNIER (*Bull. Soc. Chim.*, [3], 11,
124—125).—A method of obtaining aromatic secondary alcohols by
the action of allylic iodide and zinc on aldehydes has already been de-
scribed by the author (this vol., i, 19). He now finds that the pro-
cess is applicable to the fatty series, and that allylic bromide may be
advantageously substituted for the iodide.

Ethylallylcarbinol, $C_3H_5\cdot CHEt\cdot OH$, is obtained by the action of
allylic bromide on propaldehyde in presence of zinc turnings and dry
ether. It is a colourless liquid, boiling at 130—132°; sp. gr. =
0·843 at 18°. The *acetate*, $C_3H_5\cdot CHEt\cdot OAc$, is a colourless liquid of
an agreeable odour; it boils at 150—152°, and has sp. gr. = 0·891 at
18°.   M. O. F.

Chloralose. By A. PETIT and M. POLONOVSKI (*Bull. Soc. Chim.*,
[3], 11, 125—133).—Heffter (Abstr., 1889, 845) has already shown
that chloralose and parachloralose are dextrogyrate. The authors
have determined the rotatory power of chloralose, and find that for a
5 per cent. solution in 98 per cent. alcohol $[\alpha]_D = + 19\cdot4°$ at
20—22°, whilst a solution in 4 per cent. potash gives $[\alpha]_D = + 15°$
at the same temperature.

Contrary to the statement of Hanriot and Richet (this vol., i, 105),
both chloralose and parachloralose reduce Fehling's solution on boil-
ing, remaining indifferent towards ammoniacal silver nitrate. If,
however, ammonia be added in sufficient quantity to redissolve the
precipitate formed on adding sodium hydroxide to silver nitrate, a
solution is obtained which is reduced by chloralose at a temperature
of 70°.

Hot solutions of the alkalis eliminate chlorine from chloralose and
parachloralose with the development of a brown coloration, and a
similar result, accompanied by evolution of carbonic anhydride, is
produced by sodium carbonate. When boiled for some hours with
dilute baryta water, chloralose gives rise to products identical with
those obtained on subjecting glucose and chloral to similar treatment,
and the authors therefore conclude that under these conditions
chloralose is first split up into glucose and chloral, these substances
undergoing further decomposition in presence of the hot alkali. The
behaviour of chloralose towards dilute acids fully confirms this view.
When boiled for three hours with 20 per cent. sulphuric acid, chloral
and glucose are formed, and if hydrochloric acid is employed, the re-

action proceeds almost quantitatively; hydrolysis is also effected when chloralose is boiled with distilled water.

Owing to its insolubility, parachloralose undergoes decomposition more slowly than the isomeric compound, although identical products are obtained.

The authors consider that the ease with which chloralose is broken up into glucose and chloral points to the constitution

$$CH \underset{CH(OH)\cdot CH(OH)}{\overset{O-----CH(CCl_3)}{\diagdown}} C\cdot CH(OH)\cdot CH_2\cdot OH,$$
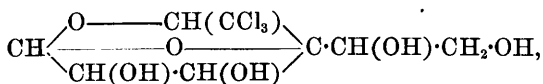
this view being in agreement with the formation of tetra-substitution derivatives by the action of acids and acid chlorides on it (*loc. cit.*). Chloralic acid, which is obtained by oxidising chloralose, is represented by the formula

$$CH \underset{CH(OH)\cdot CH(OH)}{\overset{O-----CH(CCl_3)}{\diagdown}} C\cdot COOH.$$
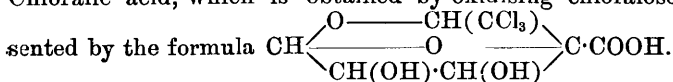
M. O. F.

Formation of Mannitol in Wines. By H. MALBOT and A. MALBOT (*Bull. Soc. Chim.*, [3], **11**, 176—179; compare this vol., i, 269).—A description of the various hypothesis put forward to explain the formation of mannitol in wines. The paper is to be continued. M. O. F.

Two new Hexitols and Compounds of the Polyvalent Alcohols with Benzaldehyde. By E. FISCHER (*Ber.*, **27**, 1524—1537). —According to theory, 10 stereoisomeric forms of hexitol should exist, but only five have been hitherto obtained, namely, two mannitols, two sorbitols and dulcitol. The author has prepared two other members of the dulcitol series: the one, from *d*-talose, which is therefore termed *d-talitol*; the other, from dulcitol, is in all probability *i-talitol*. Talonic acid is prepared by the action of pyridine on galactonic acid in the manner previously described (Abstr., 1892, 299). Hydroxymethylpyromucic acid, $OH\cdot CH_2\cdot C \underset{O-C\cdot COOH}{\overset{CH\cdot CH}{\diagdown}}$, is formed in small quantity as a bye-product; it darkens at 160°, and melts at 165—170° with evolution of gas; its formation resembles that of pyromucic acid from arabonic acid (Abstr., 1892, 437). Talonic acid is converted into a lactone on evaporation in aqueous solution, and from this d-talitol is formed by reduction with sodium amalgam; it is a colourless, slightly sweet syrup, sparingly soluble in ether. A 10 per cent. aqueous solution in a 10 cm. tube gives a refraction of +0·23°; on the addition of borax and alkali, this becomes —0·55°; these numbers are only approximate. The yield is 40 per cent. of the talonic acid employed. The *tribenzal derivative*, $C_6H_8O_6(CHPh)_3$, crystallises from alcohol in slender, colourless needles; it softens at 200°, melts at 210° (corr.), and closely resembles tribenzalmannitol.

i-Talitol is prepared by the oxidation of dulcitol by means of lead peroxide and hydrochloric acid, and subsequent reduction of the

2 *f* 2

product with sodium amalgam. It crystallises in slender, concentric needles, melts at 66—67°, and is readily soluble in water and alcohol. The *tribenzal-derivative* crystallises from alcohol in slender, colourless needles, and melts at 210° (corr.). The yield is only 2—3 per cent. of the dulcitol employed. The compound so closely resembles tribenzal-d-mannitol that it was at first thought to be *tribenzal-i-mannitol*, the latter was therefore prepared for comparison; it melts at 190—192°.

A comparison of the benzal derivatives of the polyvalent alcohols shows that whilst their composition differs considerably, they are, with the exception of benzalsorbitol and benzalglycerol, formed under similar conditions. At present, it is impossible to decide what influence the configuration of the molecule exerts on the formation of these compounds. Benzal-α-glucohepitol, $C_7H_{14}O_7$:CHPh (m. p. 218° corr.), has previously been prepared; under modified conditions, which are fully described, a labile modification is formed, which melts at 153—154° (corr., 155—156°); it is stable when dry, but under the influence of light and moisture, or on crystallisation from alcohol, changes rapidly into the stable form. The higher melting modification is readily soluble in hot water, not insoluble, as previously stated. *Dibenzaldulcitol*, $C_6H_{10}O_6(CHPh)_2$, is prepared by the interaction of benzaldehyde, dulcitol, and hydrogen chloride, or of hydrochloric acid at 0°, and crystallises from alcohol in slender needles melting and decomposing at 215—220° (uncorr.). It is readily resolved into its constituents on boiling with dilute acids. *Benzalarabitol*, $C_5H_{10}O_5$:CHPh, prepared in a similar manner to the preceding compound, crystallises from chloroform, melts at 150° (corr., 152°), and is readily hydrolysed. *Dibenzalerythritol*, $C_4H_6O_4(CHPh)_2$, crystallises in slender needles, and melts at 197—198° (corr., 201—202°). It may be conveniently used for the identification of erythritol.

Benzalglycerol, $C_3H_6O_5$:CHPh, is prepared by the action of hydrogen chloride on benzaldehyde and glycerol at 0°, and crystallises from water in colourless, stellate needles melting at 66°. It has a bitter taste, distils in a vacuum without decomposition, and is immediately hydrolysed by the action of dilute acids. The benzalglycerol prepared 30 years ago by Harnitzky and Menschutkin was impure; it differed considerably from the author's compound, with which it is possibly isomeric.

Benzaltrimethyleneglycol, $CH_2<^{CH_2 \cdot O}_{CH_2 \cdot O}>CHPh$, is prepared in a similar manner to the preceding compound, and is deposited from light petroleum in colourless crystals melting at 49—51°, and boiling at 125° (14 mm.). It is rapidly decomposed by dilute acids, but is unaffected by boiling with alkalis and phenylhydrazine in aqueous solution. J. B. T.

Compounds of the Sugars with Polyhydric Phenols. By E. FISCHER and W. L. JENNINGS (*Ber.*, **27**, 1355—1362).—It has been shown (this vol., i, 3) that the aliphatic alcohols react with certain sugars in presence of hydrochloric acid, forming glucosides; the

monohydric phenols, when subjected to the same treatment, remain unaltered. The experiments to be described show, however, that the polyhydric phenols yield compounds with certain sugars which differ widely according to the phenol employed. It has long been observed by Reichl, Molisch, Ihl, Selivanoff, Wheeler, and Tollens that various sugars give colour reactions with certain phenols in presence of hydrochloric or sulphuric acid. The products to be described are, however, colourless, and being obtained at a low temperature, the sugar molecule is preserved. The authors have not succeeded in obtaining the new substances in the crystalline condition, but having determined their composition with great probability, they are constrained to regard them as chemical individuals.

Resorcinol combines readily with all the aldoses with which the reaction has been tried; equimolecular proportions of the reagents give rise to compounds insoluble in alcohol, whilst when the amount of resorcinol is doubled, substances soluble in alcohol represent the main product.

Arabinose-resorcinol, $C_{11}H_{14}O_6$, is obtained by saturating an aqueous solution containing molecular proportions of arabinose and resorcinol with hydrogen chloride at a low temperature, and, after allowing it to remain for some hours at $0-10°$, pouring the resulting reddish liquid into absolute alcohol. The compound is an amorphous, almost colourless powder having a faint taste; it dissolves readily in water, but very sparingly in alcohol, ether, benzene, chloroform, and glacial acetic acid, and decomposes at $275°$. The compound remains unaltered when boiled with alkalis, and does not yield an osazone when heated with phenylhydrazine acetate; it exhibits, however, many reactions similar to those of resorcinol, thus: Its aqueous solution gives a bluish-violet coloration with ferric chloride, an insoluble *bromo*-derivative with bromine-water, and a colouring matter with diazobenzenesulphonic acid. Its solution in hydrochloric acid yields a condensation derivative with benzaldehyde.

Glucose-resorcinol, $C_{12}H_{16}O_7$, is obtained in a similar manner, although somewhat less readily than the arabinose derivative. It differs from the latter in being more easily hydrolysed by warm, dilute hydrochloric acid. Corresponding compounds are also obtained from xylose, galactose, and glucoheptose, but these were not analysed.

In the case of the ketoses, fructose, and sorbinose, a dark red, insoluble compound is formed, even at a low temperature, which is probably identical with the product obtained by Ihl, and later by Selivanoff (Abstr., 1887, 459).

Detection of Carbohydrates by means of Resorcinol.—The compounds of resorcinol just described give beautiful, magenta colorations when treated with oxidising agents in alkaline solution. The reaction with Fehling's solution is very delicate, and appears to be available for all carbohydrates. The *modus operandi* recommended by the authors is as follows:—To the dilute aqueous solution of the substance to be tested (2 c.c.), resorcinol ($0·2$ gram), is added to the mixture saturated with hydrogen chloride at $0°$. When the amount of carbohydrate is small, the test is allowed to remain at the ordinary temperature for 12 hours; if, however, it is large, one hour suffices.

It is diluted with water, an excess of sodium hydroxide added, and warmed with Fehling's solution, of which latter only a few drops are taken when the amount of carbohydrate is small. A reddish-violet coloration ensues, which is very characteristic; it is fugitive after a time when the liquid is largely diluted. Insoluble carbohydrates, such as starch, are triturated with water, and, after the addition of resorcinol, hydrogen chloride is passed into the cooled mixture. The reaction has been found available for the detection of small quantities of saccharose, lactose, maltose, dextrin, gum, glycogen, starch, and cotton-wool; normal urine exhibits the reaction in a marked degree. It is to be recommended as a confirmatory test to that of Molisch (Abstr., 1886, 923).

Catechol reacts with the aldoses much more slowly than does resorcinol, and in the case of the quinol, which is very sparingly soluble in concentrated hydrochloric acid, no action on the sugars was observed.

Orcinol reacts with glucose more readily than does resorcinol, but the product is insoluble in water, and apparently of a complex nature.

Arabinose-pyrogallol, $C_{11}H_{14}O_7$, is obtained in the same manner as the resorcinol derivative; it is an almost colourless compound, decomposes at 240°, behaves with alkalis as pyrogallol, and gives a beautiful blue coloration with ferrous sulphate. *Glucose-pyrogallol* was also prepared. A. R. L.

Blue Iodide of Starch. By Miss C. F. ROBERTS (*Amer. J. Sci.*, [3], **47**, 422—429).—With a view of determining between the views of Mylius (Abstr., 1887, 568) and Stocks (Abstr., 1888, 126 and 668), the authoress has experimented on this subject. When blue iodide of starch is precipitated, well washed with dilute sulphuric acid, and then iodic acid added, the solid dissolves to a colourless liquid, although the presence of free iodine therein can be proved by shaking with chloroform. A single drop of a weak solution of silver nitrate is enough to destroy the deep blue colour of a test-tube full of liquid. Both these experiments point to the discharge of colour being due to the removal of hydriodic acid rather than of iodine. The authoress has been unable to obtain an aqueous solution of iodine perfectly free from hydriodic acid. If, however, a chloroform solution of iodine is well washed with water to free it from hydriodic acid, and then immediately shaken with pure water and starch emulsion, no coloration is produced. The addition of a little hydrochloric acid, or of potassium iodide, or heating the liquid, or exposing it to sunlight (the latter two operations, of course, causing the formation of traces of hydriodic acid) at once causes the blue coloration to appear. When iodine chloride is added to starch-blue, the blue colour is discharged, but iodine at the same time set free. The reaction is probably $HI + ICl = HCl + I_2$, the hydriodic acid being taken from the starch-blue. The fact that considerable quantities of iodic acid must be added to liquids containing starch-blue before the colour is discharged is probably due to the fact that, as shown by Landolt and others, the reaction between hydriodic and

iodic acids in dilute solution is very slow, and that in an aqueous solution of iodine in the light, traces of hydriodic acid are being constantly formed. Her experiments lead the authoress to support Mylius' formula, $(C_6H_{10}O_5I)_nHI$, for starch-blue. L. T. T.

Natural Oxycelluloses. By G. DE CHALMOT (*Ber.*, **27**, 1489—1491).—The author (Abstr., 1893, ii, 430; *Amer. Chem. J.*, **16**, 218) has made experiments similar to those of Cross, Bevan, and Beadle (this vol., i, 354). The substances in plants which, on simple hydrolysis, yield furfuraldehyde, he considers to be pentosans. He has shown with regard to these that (1) both the absolute and the relative quantity increase when maize or peas germinate in the dark; (2) the quantity in the seed is partly transferred to the young plant; (3) in the germination of the seeds of *Tropæolum majus* the absolute amount decreases; (4) the percentage amount increases in various organs of living plants; (5) the percentage amount shows no regular decrease or increase after the lignification is complete; (6) in the case of 30 different trees, the presence of these substances is not essential to lignification. C. F. B.

New Constituents of Wood Oil. By E. LOOFT (*Ber.*, **27**, 1542—1546; compare Abstr., 1893, i, 558).—The author has succeeded in separating the following compounds from crude wood oil; they were identified by their boiling points, the analytical results, and the preparation of characteristic derivatives: methylpyridine, dimethylpyridine, (iso)butylic alcohol, pimelic ketone, and an alcohol of the formula $C_8H_{14}O$. Full details of the methods of separation employed are given in the original paper. The sp. gr. of pimelic ketone $= 0.9416$, refractive coefficient for sodium light $= 1.443$ at $24°$; the molecular refractive power $= 27.58$. J. B. T.

Nitramines. By A. LACHMAN and J. THIELE (*Ber.*, **27**, 1519—1520).—The nitramines of several of the simplest of the acid amides cannot be obtained by the method adopted by Franchimont (*Rec. Trav. Chim.*, **2**, 95, 340; **3**, 219) for the preparation of other nitramines. If, however, only the theoretical amount of nitric acid be taken, the nitrate of the amide being employed when one exists, these derivatives can be prepared quite readily.

Nitrocarbamide, $NO_2 \cdot NH \cdot CO \cdot NH_2$, is precipitated when a solution of carbamide nitrate in sulphuric acid is poured upon ice. It forms a powder, which is sparingly soluble in cold water and alcohol, more readily on warming. It is a strong acid, expels carbonic anhydride, and forms neutral alkali salts. When warmed with alkalis, it is decomposed and gas is evolved; mercuric and mercurous nitrates produce sparingly soluble compounds. When reduced, it yields a small amount of semicarbazide.

Nitro-urethane, $NO_2 \cdot NH \cdot COOEt$, is obtained by adding the calculated amount of nitric acid to a solution of urethane in sulphuric acid. It crystallises from light petroleum in splendid plates, melts at $64°$, and is readily soluble in most solvents. An *ammonia* derivative $NH_3,NO_2 \cdot NH \cdot COOEt$, melts at $183°$.

Dicyanodiamide and biuret yield similar derivatives, which are being further investigated.   A. H.

Isonitramines. By W. Traube (*Ber.*, **27**, 1507—1510).—When dry nitric oxide is passed into a 10 per cent. alcoholic solution of ethylic sodacetoacetate, the gas is absorbed, and a sodium salt is precipitated. This salt separates from aqueous solution on the addition of alcohol and ether in white, lustrous plates, of the composition $C_6H_8N_2O_5Na_2 + H_2O$. It is very readily soluble in water, yielding an alkaline solution. Silver nitrate produces a white precipitate, which decomposes with evolution of gas and separation of silver when the liquid is heated. The sodium salt decomposes with a gentle explosion when it is heated. Dilute acids decompose the salt slowly in the cold, violently when heated, a mixture of nitrogen and nitrous oxide being evolved. This salt probably belongs to the same class of substances as the salts of dinitrososulphonic acid, $H_2N_2SO_5$, and of the dinitroalkylic acids, such as EtN_2O_2H. It has the composition of a nitramine, and may, therefore, be provisionally termed an *isonitramine*.

Similar compounds may be obtained from ethylic benzoylacetate, ethylic malonate, benzoylacetone, and monoketones, such as acetone.

The *acetone*-compound, $CH_2(N_2O_2Na)_2$, is formed, together with sodium acetate, when nitric oxide is passed into an alcoholic solution of acetone to which caustic soda or sodium ethoxide has been added. A yellow sodium salt is formed from which the *barium* salt, $CH_2(N_2O_2)_2Ba + 3H_2O$, may be prepared. This forms lustrous, colourless needles, and is almost insoluble in cold water, but dissolves sparingly in hot water yielding a neutral solution. The dry compound explodes when heated, and is decomposed by acids. Acetophenone yields the same compound along with benzoic acid. The substance, $CH_2(N_2O_2)_2H_2$, from which these salts are derived, may be termed *methylenedi-isonitramine*. The investigation of these compounds is being continued.   A. H.

Dimethylarsine. By A. W. Palmer (*Ber.*, **27**, 1378—1379).— *Dimethylarsine*, $AsHMe_2$, has been obtained, for the first time, by reducing cacodyl chloride with platinised zinc and alcoholic hydrogen chloride. It is a colourless, mobile liquid, boiling at 36—37° (uncorr.); it inflames spontaneously in air, and is decomposed by silver nitrate solution, silver being precipitated and, apparently, cacodylic acid formed.   C. F. B.

Natural Unsaturated Ketone. By P. Barbier and L. Bouveault (*Compt. rend.*, **118**, 983—986).—Oil of lemon grass, according to Dodge, contains geranaldehyde, $C_{10}H_{16}O$. The authors find that by fractionation under a pressure of 12 mm. the oil can be separated into a fraction boiling at 67—75°, another boiling at 110—115°, and a third consisting of a brown, viscous liquid, which has not yet been investigated. The lowest fraction, which under ordinary pressure distils completely at 170—175°, is generally regarded as consisting of a terpene, but the authors find that it usually consists of a mixture of

a non-saturated ketone and a terpene. The ketone when separated by means of the bisulphite compound, has the composition $C_8H_{14}O$, and boils at 169—170° under ordinary pressure; sp. gr. at $0 =$ 0·8632; refractive index at 15·6°, $n_{645} = 1·4608$, $n_{452·6} = 1·4760$; molecular weight by Raoult's method, 125·7. With potassium iodide and sodium hypobromite the ketone yields iodoform, and this, together with the formation of a bisulphite compound, indicates the presence of the ·COMe group. With chromic acid mixture, the ketone yields carbonic anhydride, acetone, formic acid, and acetic acid, and hence it would seem that it is *methyl hexylene ketone*, $CMe_2:CH·CH_2·CH_2·COMe$. It differs in chemical and physical properties from the methyl hexylene ketone obtained by synthesis (this vol., i, 224), and is not identical with that obtained by Wallach by the distillation of cinoleic anhydride, nor with that obtained by Tiemann and Semmler by the oxidation of geraniol and geraldehyde.

The terpene sometimes associated with this methyl hexylene ketone, boils at 175°, and has a rotatory power $[\alpha]_D = -5° 48'$. It combines with exactly 4 atoms of bromine, but the bromo-derivative yields only a very small quantity of crystals melting at 85°, and hence the terpene is not a limonene. The absence of this terpene in some cases, and the great variation in its proportions in others, indicates that it is added for the purpose of adulteration. C. H. B.

The Aldehyde from Oil of Lemon grass. By P. BARBIER and L. BOUVEAULT (*Compt. rend.*, **118**, 1050—1052).—When geranaldehyde is treated with chromic acid mixture at a low temperature, it yields formic and acetic acids and a methylhexyleneketonecarboxylic acid, $C_8H_{13}O·COOH$, which yields iodoform when mixed with potassium iodide and sodium hypobromite. This acid would seem to be identical with the oily acid obtained by Tiemann and Semmler, which yielded methyl hexylene ketone when distilled.

When oxidised by means of boiling chromic acid mixture, geranaldehyde yields carbonic anhydride, acetone, acetic acid, and terebic acid, $C_7H_{12}O_5$. When boiled with three times its weight of glacial acetic acid for 24 hours, geranaldehyde is converted into cymene.

It would follow from these reactions that geranaldehyde has the constitution $CH_2:CMe·CH_2·CH_2·C·(COH):CMe_2$, and not that ascribed to it by Tiemann and Semmler (this vol., i, 82). Its conversion into cymene can be explained by assuming that the acetic acid first acts as a hydrating and afterwards as a dehydrating agent. C. H. B.

Crystallographic Properties of the two Stereoisomeric α-Methyl-β-chlorocrotonic acids from α-Dichloro-s-dimethylsuccinic acid. By R. OTTO (*Ber.*, **27**, 1351—1352).—The α-methyl-β-chlorocrotonic acid melting at 50—60° (this vol., i, 318) crystallises from water in six-sided, biaxial laminæ showing straight extinction; it therefore does not answer the description given by Brugnatelli and by Kloos.

The isomeric acid melting at 73° is obtained in transparent, glassy, monosymmetric crystals of variable habit:

$$a : b : c = 0.9232 : 1 : 1.2421. \quad \beta = 83° 23'.$$

These results agree with those of Kloos.   W. J. P.

Formation of Pyruvic acid in an Aqueous Solution of Tartaric acid independently of Micro-organisms. By R. OTTO (*Ber.*, **27**, 1264—1265).—A careful examination of the solution of tartaric acid which contained pyruvic acid after being kept for some years (this vol., i, 274), has proved the absence of micro-organisms.
                                                           E. C. R.

Preparation of Glyoxylic acid. By C. BÖTTINGER (*Arch. Pharm.*, **232**, 65—69).—Debus's method of preparing glyoxylic acid is modified in regard to the proportions of alcohol and nitric acid employed, 50 c.c. of absolute alcohol being separated by a layer of 27 c.c. of water from 100 c.c. of nitric acid (sp. gr. 1·48) at 5°; when complete mixture has taken place, ethylic nitrite is removed by distillation, and glyoxylic acid can then be separated from the residual liquid in the usual manner.

A *calcium salt* of the formula $(C_2H_3O_4)_2Ca + H_2O$ separates slowly from cold dilute solutions; it becomes anhydrous at 110°. When boiled with acetic anhydride, glyoxylic acid forms an *acetate*, a gum-like substance which is gradually resolved into acetic acid and glyoxylic acid by cold water.   M. O. F.

Detection of Glyoxylic acid. By C. BÖTTINGER (*Arch. Pharm.*, **232**, 1—3).—Glyoxylic acid forms with dimethylaniline a colourless condensation product, readily soluble in a dilute solution of caustic soda, from which it is precipitated by dilute acetic acid in slender, colourless needles; when boiled with an aqueous solution of mercuric chloride, a deep blue coloration is developed.

The liquid obtained by warming glyoxylic acid and resorcinol with a small quantity of absolute alcohol, gives, on dilution with water and careful addition of ammonia, a deep blue colour which soon becomes bright red; when caustic soda is employed, the final tint is cherry red. If a mixture of glyoxylic acid and resorcinol is heated on a water bath with concentrated sulphuric acid, evolution of carbonic anhydride takes place, and a substance is obtained which is scarcely soluble in water or dilute caustic soda.

An ammoniacal solution of the compound formed on adding glyoxylic acid to β-amidoalizarin dissolved in concentrated sulphuric acid, has a deep violet-red colour. A brown, crystalline substance has been obtained by adding glyoxylic acid to an alcoholic solution of α-naphthylamine.

The author has studied the action of ammonium hydrosulphide on dichloracetic acid, obtaining a *lead salt* of the constitution

$$(CHS·COO)_2Pb.$$

The acid formed on decomposing this salt with hydrogen sulphide or sulphuric acid is extremely volatile and unstable. It gives rise to a volatile *ethylic salt*, which possesses a penetrating, garlic-like odour, and forms a colourless compound with phenylhydrazine.

                                                           M. O. F.

Conversion of Ethylic Dioxysuccinate into Ethylic Oxymalonate and Ethylic Oxalate by elimination of Carbonic Oxide. By R. ANSCHÜTZ and H. PAULY (*Ber.*, **27**, 1304—1306).—In the preparation of ethylic dioxysuccinate from sodium tetrahydroxysuccinate, alcohol, and hydrogen chloride, the authors observed that, during the distillation of the product, decomposition set in, and ethylic oxymalonate and ethylic oxalate were formed. The same two compounds are most easily obtained from ethylic dioxysuccinate by heating it at 125° under a pressure of 12 mm. with a small quantity of the tarry residue obtained in a previous decomposition. The same decomposition takes place less readily when ethylic dioxysuccinate is heated alone at 280—290°. Carbonic oxide is evolved in large quantities during the decomposition. When ethylic oxymalonate is heated at 180° under 12 mm. pressure, carbonic oxide is evolved and ethylic oxalate is formed.

Ethylic dioxysuccinate, oxymalonate, and oxalate are therefore the first members of an homologous series of compounds in which the homology is determined by the carbonyl group. E. C. R.

Anomalous Condensations. By C. A. BISCHOFF and P. WALDEN (*Ber.*, **27**, 1491—1495).—Reactions have been studied in which condensation takes place accompanied by linkage (i) of C with C, as in the case of ethylic sodiomethylmalonate with ethylic α-bromisobutyrate; (ii) of C with N, as of (*a*) piperidine with ethylic α-bromopropionate, or of (*b*) aniline with chloracetamide; (iii) of C with O, as of sodium orthonitrophenoxide with ethylic α-bromopropionate. Many anomalous cases were observed; these may be put into three categories : (**A**) the condensation takes place, not at the α- but at the β-position, or mainly in this position; (B) condensation takes place not between unlike, but between two like molecules; (C) no condensation occurs. The paper is a preliminary one, and must be consulted for further details. C. F. B.

Behaviour of Maleïc acid on heating. By S. TANATAR (*Ber.*, **27**, 1365—1368).—The author's experiments show that when maleïc acid is heated with benzene, it is directly converted into fumaric acid ; maleïc anhydride and, consequently, also water are likewise produced. The formation of malic acid observed by Skraup (this vol., i, 15) is to be attributed to the interaction of fumaric acid and water at the high temperature. Contrary to Skraup's observation, when dry maleïc acid is heated at 180—190°, no malic acid is found. A. R. L.

Conversion of Citraconic acid into Mesaconic acid. By R. FRANZ (*Monatsh.*, **15**, 209—227).—The author has carried out with citraconic acid experiments similar to those made by Skraup (Abstr.. 1891, 1338 ; and this vol., i, 15) with maleïc acid. When an aqueous solution of citraconic acid was heated at 120°, some itaconic acid was formed ; when heated at 180—200°, it was partially converted into mesaconic acid. Neither at these nor intermediate temperatures could any change of titre (formation of lactone) be observed. Neither hydrogen sulphide nor sulphurous anhydride alone has any effect on citraconic acid, but when these two compounds are allowed

to act together on a solution of the acid, a small proportion thereof is converted into mesaconic acid. When the copper and lead salts are decomposed by hydrogen sulphide, mesaconic acid is formed in small quantities, the lead salt yields, however, much less than the copper salt. No mesaconic acid was formed by heating copper citraconate to incipient decomposition.

Mineral acids act much more energetically in bringing about this change, the quantity of mesaconic acid formed being larger the stronger the solution of mineral acid, the greater the proportion of such solution used, and the longer the heating is continued. The amount of conversion is in all cases much smaller than is the case with maleïc acid.

For the purpose of this research, the author investigated the methods of separation of itaconic, citraconic, and mesaconic acids. He found that the data generally given as to the behaviour of these acids to steam distillation are incorrect, for whilst citraconic acid is much the most volatile in steam, the other two acids also pass over in quantities too appreciable to enable this method to be used for quantitative separation. The author took advantage of the different solubilities of these acids in water and ether. In water, mesaconic is by far the least soluble, citraconic by far the most soluble, whilst in ether the order of solubility is exactly reversed. By treating an aqueous solution containing the mixed acids with its own volume of ether, almost the whole of the mesaconic acid, and but very little of the citraconic acid is removed. The ether is distilled off, the residue dried over sulphuric acid and any citraconic acid removed by rubbing on a porous plate with a trace of water or by washing with a concentrated solution of mesaconic acid. The percentage of mesaconic acid so obtained is always much below that present, but the process is available as an indication of the relative quantities converted in different reactions.   L. T. T.

Propionyl Derivatives of Ethylic Mucate. By P. FORTNER and Z. H. SKRAUP (*Monatsh.*, **15**, 200—208).—When ethylic mucate is digested in a reflux apparatus with propionic chloride, *ethylic tetrapropionylmucate*, $COOEt \cdot [CH \cdot O \cdot COEt]_4 \cdot COOEt$, is obtained, which forms colourless transparent crystals, melts at 118—120°, and is easily soluble in ether, acetone, benzene, glacial acetic acid, and boiling alcohol. If the digestion is carried on, however, in sealed tubes at 100°, *ethylic tripropionylmucolactone*, $COOEt \cdot [CH \cdot O \cdot COEt]_3 \cdot CH {<}^{O}_{CO}{>}$, is formed, together with some of the tetrapropionyl compound. This lactone yields colourless crystals, melting at 56—58°, and easily soluble in ether. The constitution of these two compounds was established by estimations of the propionyl and ethoxyl groups. When hydrolysed with acids, both yielded mucic acid, and with alkalis the isomeric acids found by Skraup (this vol., i, 16) in the similar treatment of ethylic tetracetylmucate were obtained.

In view of these results the authors have re-examined the corresponding acetyl reaction (*loc. cit.*), and find that the compound then described by Skraup as β-ethylic tetracetylmucate is really ethylic

triacetylmucolactone, for which the percentage composition is almost identical with that of the tetracetyl compound. L. T. T.

Method for obtaining Carbamides containing Tertiary Alkyl Radicles. By A. SCHNEEGANS (*Arch. Pharm.*, **231**, 675—680).—The method consists in heating the bromide of the tertiary alcohol with a mixture of white lead (as a source of lead hydroxide) and carbamide.

Tertiary butylcarbamide $NH_2 \cdot CO \cdot NH \cdot CMe_3$, crystallises in needles, melts and partially decomposes at 172°, and dissolves sparingly in cold water, but freely in alcohol.

Tertiary amylcarbamide, already described by Würtz, was similarly prepared; it melts at 151—152°; its crystallography is described.

Tertiary heptylcarbamide, $NH_2 \cdot CO \cdot NH \cdot CEt_3$, crystallises in needles, decomposes at 150°, and is nearly insoluble in cold water, but fairly soluble in boiling water.

The solubility of these carbamides in cold water decreases with increase of molecular weight, the proportion of water requisite for the solution of one part of each of the three respectively, in the above order, being 46·3, 79, and 410 parts. A. G. B.

Methylketopentamethylene and its derivatives, and Symmetrical Ketopentamethenylene. By E. LOOFT (*Ber.*, **27**, 1538—1542).—An additive compound of sodium hydrogen sulphite with α-methyl-β-ketopentamethenylene, has been previously described (Abstr., 1893, i, 558), from this the ketone is regenerated on heating with acids, or by the action of alkalis at ordinary temperatures.

1-*Methyl*-5-*hydroxypentamethylene*, $CHMe<^{CH(OH) \cdot CH_2}_{CH_2 \underline{\quad\quad} CH_2}$, is formed by the reduction of the keto-compound with sodium in moist ethereal solution, it is a colourless mobile liquid, with an odour resembling that of iodoform, it boils at 148—149°; the sp. gr. = 0·9273 at 14·5°; the coefficient of refraction for sodium light = 1·4475; molecular refractive power = 28·84.

The *pinacone* $^{CH_2 \cdot CH_2}_{CH:CMe}>C(OH) \cdot C(OH)<^{CH_2-CH_2}_{CMe:CH}$ is obtained with the preceding compound, and is a thick, pale yellow liquid boiling at 330°, and remaining liquid at −20°. The *hydroxynitrile*,

$$^{CH_2 \cdot CH_2}_{CH:CMe}>C(OH) \cdot CN,$$
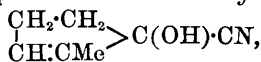
is prepared by the action of hydrogen cyanide on the ketone in aqueous solution, it crystallises in long needles, melts at 49°, boils at 213° under 300 mm. pressure, and, with slight decomposition, at 240° (corr.) under ordinary pressures. The *hydroxy acid*,

$$^{CH_2 \cdot CH_2}_{CH:CMe}>C(OH) \cdot COOH,$$
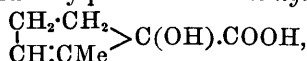
is formed quantitatively from the nitrile by hydrolysis with hydrochloric acid, it is crystalline, very readily soluble, and melts at 87—88°. The salts are amorphous and readily soluble.

Symmetrical ketopentamethenylene, $CO < \begin{array}{c} CH_2 \cdot CH \\ | \quad | \\ CH_2 \cdot CH \end{array}$, prepared by the distillation of calcium Δ^3-dihydromuconic acid, is a colourless liquid, and, like the oxime, readily combines with bromine. The *oxime* and its *hydrochloride* are oily. J. B. T.

Hexachlorobenzene Dichloride. By E. BARRAL (*Compt. rend.*, **118**, 1049).—When hexachlorophenol, C_6Cl_6O, is heated in a sealed tube at 150—155° for 24 hours with phosphorus pentachloride, *hexachlorobenzene dichloride*, C_6Cl_8, is formed, and is purified by crystallisation from light petroleum. It forms long, colourless prisms, which melt to a colourless liquid at 159—160°, but decompose into chlorine and hexachlorobenzene at a higher temperature. It dissolves readily in anhydrous ether, benzene, and alcohol, especially on heating, and is also somewhat soluble in hot light petroleum. A boiling aqueous solution of sodium hydroxide neither dissolves nor decomposes it; fuming nitric acid dissolves it slowly on heating, and when water is added a white precipitate separates and the liquid contains chlorine.
C. H. B.

Derivatives of Pseudocumene. By R. NIETZKI and J. SCHNEIDER (*Ber.*, **27**, 1426—1432).—*Dinitrochloropseudocumene*, $C_6Me_3Cl(NO_2)_2$, is prepared by the direct nitration of chloropseudocumene,

$$C_6H_2Me_3Cl(1:3:4:6),$$
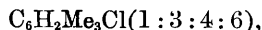
and forms almost colourless needles, melting at 205—206°. Although this substance contains a chlorine atom in the ortho-position to a nitro-group, it does not react with alcoholic ammonia or aniline. *Paradiamidochloropseudocumene* forms slender needles, melting at 171°. When a solution of a salt of this base is treated with ferric chloride, *chloropseudocumoquinone* is obtained in slender golden-yellow needles, melting at 72—73°. Sulphurous acid reduces it to the *quinol*, which melts at 202°, a *quinhydrone*, melting at 154°, being formed as an intermediate product in dark needles with a metallic lustre. The quinol yields a *diacetate* melting at 172°.

Paradinitropseudocumene is prepared from dinitropseudocumidine by the diazo-reaction; it forms orange-yellow needles, melting at 96°. *Paradiamidopseudocumene* was obtained in the form of the hydrochloride by the reduction of the foregoing substance. On oxidation, it yields a *pseudocumoquinone*, which crystallises in long yellow needles, and melts at 32°, and thus differs from that obtained by Noelting and Baumann (*Ber.*, **18**, 1152) from isoduridine, which melted at 11°. On reduction, it is converted into a quinol, which melts at 170°, and is apparently identical with that obtained by Noelting and Baumann. The *diacetate* melts at 112°. The difference between the two quinones is probably due to some impurity in that prepared from isoduridine. *Pseudocumoquinonoxime* crystallises in long golden-yellow needles, and melts at 184°. A dioxime could not be obtained. Pseudocumoquinonoxime may have either of the following formulæ:

[$Me_3 : O : NOH = 1 : 3 : 4 : 5 : 2$ or $1 : 3 : 4 : 2 : 5.$]
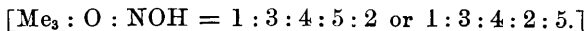
In order to decide this question, pseudocumenol,

$$C_6H_2Me_3 \cdot OH[1:3:4:5],$$
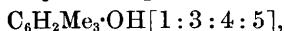
was treated with nitrous acid. The nitroso-compound thus produced, which must have the constitution shown by the first formula, melts at 134°, and is odourless, and therefore differs from the pseudocumoquinoxime, which, as stated above, melts at 184°, and, moreover, has an intense odour of quinone. This substance seems therefore to have the second of the two formulæ. A. H.

Additive Products of the Aromatic Isocyanides. By W. R. SMITH (*Amer. Chem. J.*, **16**, 372—393).—Paratolylic isocyanide is a colourless crystalline solid, which melts at 21° to a colourless oil, and boils at 99° under 32 mm. pressure. Its odour is less disagreeable than that of phenylic isocyanide; its taste is extremely bitter. In the liquid form, it soon decomposes and polymerises, but is fairly stable in the solid form. Sulphur (in carbon bisulphide solution at 120—140°) converts it into the corresponding thiocarbimide, melting at 26° and boiling at 242—243°. The tendency to form this compound is so great that the isocyanide will take up sulphur from a carbon bisulphide solution of bromine and from vulcanised indiarubber.

The isocyanide interacts with sulphur monochloride to form the thiocarbimide and *paratolylimidocarbonic chloride,* $C_6H_4Me \cdot N:CCl_2$.

With hydrogen sulphide, in alcoholic solution at 100°, the isocyanide yields *paratolylimidothioformic acid,* $C_6H_4Me \cdot N:CH \cdot SH$, which crystallises in nearly colourless flat needles, and melts at 175—176°. With ethylmercaptan at 100°, it yields the *ethylic salt* of this acid, a slightly yellow oil of disagreeable odour, boiling at 250—252°.

With alcoholic sodium ethoxide at 120°, the isocyanide yields *ethylic paratolylimidoformate,* $C_6H_4Me \cdot N:CH \cdot OEt$, a pleasant-smelling yellow oil, which boils at 231—232° under 743 mm. pressure, and solidifies to a crystalline substance, melting at 8°. The *methylic salt* is made in a similar manner, and boils at 216—218°. Both salts are converted by hydrochloric acid into diparatolylformamidine hydrochloride. The amidine also results from direct interaction between the isocyanide and paratoluidine at 200°, or alcoholic paratoluidine at the ordinary temperature.

The isocyanide is reduced by nascent hydrogen (sodium in amylic alcohol) to methylparatoluidine.

Paratolylic isocyanide interacts with carbonic chloride in ethereal solution at −18° to form *mesoxalodiparatoluidide hydrate,*

$$C(OH)_2[C(OH):N \cdot C_6H_4Me]_2;$$
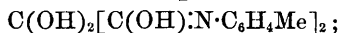
this crystallises in colourless needles and melts at 120—130° when quickly heated. When slowly heated, it loses its water of hydration and melts at 187°. It has slightly acid properties as it dissolves in alkalis, and is reprecipitated by acids. With alcohol, it forms the corresponding *alcoholate.* This, on heating, loses alcohol and leaves the anhydrous amide. The latter interacts with phenylhydrazine, but the product has not been examined.

With benzoic chloride, the isocyanide reacts at 100° to form *benzoylformoparatoluidide,* $COPh \cdot C(OH):N \cdot C_6H_4Me$, which crystallises in

yellow needles and melts at 111—113°; with acetic chloride it forms *pyruvoparatoluidide*, OH·CAc:N·C₆H₄Me. This crystallises in colourless scales and melts at 108°; it forms a polymeride melting at 193—194°. The *phenylhydrazone* melts at 204°. With formic acid the isocyanide yields formoparatoluidide.

Paratoylic isocyanide forms, with silver cyanide, a crystalline molecular compound, 2AgNC,3C₇H₇NC, which melts and decomposes at 118°.

Isocyanides easily take up two atoms of chlorine, forming alkylated imidocarbonic chlorides, and these interact with sodium alkyloxides to form alkylated imidochloroformates and imidocarbonates. *Phenylimidocarbonic chloride*, NPh:CCl₂, is most conveniently made by the action of chlorine on the thiocarbamide.

Ethylic phenylimidochloroformate, NPh:CCl·OEt, is best obtained by mixing an alcohol-ether solution of the carbonic chloride with alcoholic sodium ethoxide. It is a colourless, sweet-swelling oil, which boils at 105° under a pressure of 12 mm., and has a sp. gr. of 1·144 at 12°. It is violently decomposed by strong hydrochloric acid into phenylic isocyanate and ethylic chloride. The isocyanate undergoes a secondary change into carbanilide. The *methylic salt* boils at 104° under 15 mm. pressure and at 215°, decomposing slightly, under ordinary pressure. The *phenylic salt* boils at 168° under 12 mm. pressure, and solidifies to a white substance, melting at 43°. It is hydrolysed by hydrochloric acid into phenylic phenylcarbamate. With aniline, it forms α-triphenylguanidine. When double the quantity of sodium ethoxide required to form the chloroformate is used, *diethylic phenylimidocarbonate*, NPh:C(OEt)₂, is obtained as a colourless, and nearly odourless, oil, which boils and decomposes slightly at 245°. It is hydrolysed by cold dilute hydrochloric acid into aniline and ethylic carbonate. The *methylic salt* boils at 123·5° under 16 mm. pressure. It interacts with aniline to form carbanilide.

<div align="right">JN. W.</div>

Diphenylic Thiocarbonate. By H. ECKENROTH and K. KOCK (*Ber.*, **27**, 1368—1371).—*Diphenylic thiocarbonate*, CS(OPh)₂, is obtained by dropping thiocarbonic chloride into an aqueous solution of sodium phenoxide; it crystallises from alcohol in white leaflets, melts at 106°, boils and decomposes slightly at 336—340°, and is insoluble in water. When heated with bromine and water at 120°, a *dibromo*-derivative, C₁₃H₈Br₂O₂S, is obtained; this forms white needles, melts at 177°, and gives parabromophenol on hydrolysis with soda. By the action of ammonia or amines on diphenylic thiocarbonate, carbamide derivatives are obtained. When heated with sodium ethoxide, it yields ethylic sulphide, phenol and carbonic anhydride. *Phenylic phenylthiocarbamate*, C₁₃H₁₁NSO, is obtained by distilling diphenylic thiocarbonate with thiocarbanilide, and allowing the oily product to remain for two months; it forms white crystals, and melts at 147°. When diphenylic thiocarbonate is heated with paraditolylthiocarbamide, *paratolylthiocarbimide* and phenol are the products. Diphenylic carbonate (m. p. 78°) is formed when mercuric oxide is added to fused diphenylic thiocarbonate.

<div align="right">A. R. L.</div>

Synthesis of Benzoylphloroglucinol Trimethyl Ether. By G. CIAMICIAN and P. SILBER (*Ber.*, **27**, 1497—1501; compare this vol., i, 255).—Benzoylphloroglucinol trimethyl ether, $C_6H_2(OMe)_3 \cdot COPh$, may be synthetically obtained by heating phloroglucinol trimethyl ether in benzene solution with benzoic chloride and zinc chloride. It melts at 115°, and has all the properties of the naturally occurring methylhydrocotoïn or benzoylhydrocoton (m. p. 113°). It crystallises, however, in large plates, whilst the natural product usually occurs in needles or prisms. A crystallographic comparison of the two products shows that the constants of the two types of crystal are identical. Both the natural and the synthetical products usually crystallise in monosymmetric forms, but also sometimes occur in rhombic crystals of the same melting point.

Dibenzoylphloroglucinol trimethyl ether, $C_6H(OMe)_3(COPh)_2$, is obtained when an excess of benzoic chloride is used, and forms white needles, melting at 179°. It is sparingly soluble in alcohol, insoluble in water and alkalis, and gives no coloration with nitric acid.

The authors give the name of coto-substances to those constituents of coto bark which are derived from phloroglucinol, the constituents derived from phenylcoumalin being known as paracoto-substances.

A. H.

Reduction of Nitro-compounds. By A. WOHL (*Ber.*, **27**, 1432—1437).—The author has obtained results similar to those described by Bamberger (this vol., i, 373). The reduction of nitrobenzene by the aid of zinc-dust and water proceeds much more readily when the nitrobenzene is dissolved in alcohol of 60 per cent. and about 10 per cent. of calcium chloride added. The mass boils up at each addition of the zinc-dust, and by using the calculated amount of zinc-dust, a yield of about 75 per cent. on the nitrobenzene is obtained. The calcium chloride appears to aid the reaction by forming an insoluble basic salt with the zinc hydroxide, and thus preventing it from hindering the course of the reduction. The phenylhydroxylamine thus obtained has already been described by Bamberger. It readily combines with aldehydes and with phenylthiocarbimide, yields ethylic derivatives with ethylic iodide and sodium ethoxide, and is converted by nitrous acid into the sparingly soluble *nitrosophenylhydroxylamine*, $OH \cdot NPh \cdot NO$. This forms slender, white needles, melts without decomposing at 58—59°, and decomposes at 75°. It is a strong acid, dissolves in alkalis, and expels carbonic anhydride from aqueous sodium carbonate when heated. Warm acids decompose it with formation of nitrosobenzene, but it is very stable in alkaline solution, even on boiling. Under the same conditions, finely-divided metallic iron also acts on nitrobenzene as a powerful reducing agent, but the final product of the reaction is aniline. The author considers that in the technical reduction of nitrobenzene the function of the hydrochloric acid is to produce a certain amount of ferrous chloride, which then acts in a similar manner to the calcium chloride employed in his experiments. A. H.

Nitrites of certain Amines. By W. A. Noyes and H. H. Ballard (*Ber.*, **27**, 1449—1451).—Hexamethylenediamine nitrite is decomposed, by prolonged boiling in aqueous solution, into Δ^3-tetrahydroaniline, 1 : 4-amidohydroxyhexamethylene, and dihydrobenzene; the last was recognised by its smell and the characteristic coloration with sulphuric acid and alcohol. Δ^3-*Tetrahydroaniline platinochloride* crystallises from alcohol in yellow plates melting at 210° with decomposition. 1 : 4-*Amidohydroxyhexamethylene platinochloride* crystallises in flat, lemon-coloured plates, and is converted into the preceding compound by heating at 135°. Δ^3-Tetrahydroaniline nitrite is more stable than hexamethylenediamine nitrite; after boiling for 25 minutes, only 16 per cent. was decomposed. β-Tetrahydronaphthylamine is the analogue of Δ^3-tetrahydroaniline; the nitrite melts at 137°, and slowly decomposes on boiling; the chloride melts at 242—243°; the nitrate at 215°. Bamberger and Lodter state (*Ber.*, **21**, 854) that the nitrite is stable towards boiling water; their substance (m. p. 160°) is proved to be a mixture of nitrite and nitrate; they also give the melting point of the chloride as 237°. 2 : 5-Diamidohexane nitrite undergoes rapid decomposition on heating in aqueous solution. The authors point out that these observations tell against the "centric" benzene formula.   J. B. T.

Stereoisomeric Anil-compounds. By W. v. Miller and J. Plöchl (*Ber.*, **27**, 1296—1304).—In the preparation of ethylidenaniline by shaking a mixture of aniline, acetaldehyde, and water, the chief product is the ethylidenaniline melting at 126°, but a small quantity of an isomeric compound melting at 85·5° is obtained. The two isomerides are separated by means of cold alcohol in which the base melting at 85·5° is soluble. The new base crystallises in long, thin, lustrous needles, has the same molecular weight as the ordinary modification, and, with nitrous acid, yields a nitroso-compound. When heated at 100°, it remains unaltered; at 120—130°, it is converted into the isomeride melting at 126°, and at 195° it is mostly converted into quinaldine-derivatives. It is most easily converted into the high melting modification by adding a small quantity of iodine to the ethereal solution and allowing the mixture to remain, or warming on the water bath. The same conversion takes place when the ethereal solution is treated with hydrogen chloride at 0°. When treated with benzoic chloride, it yields a small quantity of benzanilide, the benzoyl-compound of the high melting base which melts at 218°, and the *benzoyl*-compound of the new base which melts at 156° and crystallises in beautiful, rectangular tablets. When treated with acetic anhydride, it yields an *acetyl*-derivative which is an amorphous, yellow powder, whereas the ordinary modification (m. p. 126°) yields an acetyl-derivative which crystallises in beautiful needles and melts at 188°. When aniline hydrochloride and acetaldehyde react with one another in aqueous solution, the product consists of two-thirds ethylidenaniline (m. p. 126°) and one-third of the new modification. The best method of preparing the new modification is from aniline acetate and acetaldehyde in aqueous solution. Aniline sulphate and acetaldehyde yield only a small quantity of the new base.

E. C. R.

Derivatives of α-Diphenylsemicarbazide and of α-Diphenyl-thiosemicarbazide. By T. VAHLE (*Ber.*, **27**, 1513—1519).—Phenyl-thiocarbimide unites directly with phenylhydrazones and with acid phenylhydrazides to form compounds which are probably derivatives of α-diphenylthiosemicarbazide, NHPh·CS·NPh·NH₂, which is, itself, unknown. Analogous compounds are formed by phenylcarbimide and the acid phenylhydrazides.

Benzylidenehydrazonediphenylthiosemicarbazide,

NHPh·CS·NPh·N:CHPh,

forms faintly yellow-coloured needles, melts at 182°, and is insoluble in hydrochloric acid and dilute soda. It only reduces Fehling's solution after vigorous boiling.

The corresponding *acetone*-derivative, NHPh·CS·NPh·N:CHMe₂, forms thick, white needles, melts at 160°, and is soluble in warm hydrochloric acid. It does not act on Fehling's solution even when boiled with it.

Acetyl-α-diphenylsemicarbazide, NHAc·NPh·CO·NHPh, is obtained by heating acetylphenylhydrazine with phenylcarbimide. It forms small, white needles melting at 175—176°, and reduces Fehling's solution on boiling. An isomeric compound, melting at 183°, which is probably *acetyl-β-diphenylsemicarbazide,* NPhAc·NH·CO·NHPh, is formed when diphenylsemicarbazide is treated with acetic anhydride.

Acetyl-α-diphenylthiosemicarbazide, NHAc·NPh·CS·NHPh, forms very pale yellow needles melting at 131—132°.

Formyl-α-diphenylsemicarbazide, NHPh·CO·NPh·NH·COH, closely resembles the acetyl-compound, and melts at 171—172°. The corresponding *thio-compound* crystallises in white needles melting at 128—129°.

Butyryl-α-diphenylsemicarbazide forms small needles melting at 155°, whilst the corresponding *thio*-compound melts at 117—118°. Butyrylphenylhydrazide may be most conveniently prepared by adding butyric chloride to a dilute ethereal solution of phenylhydr-azine (2 mols.); phenylhydrazine hydrochloride is precipitated, and the solution of the hydrazide may then be evaporated. The compound melts at 103—104° (stated as 113—114° by Michaelis and Schmidt, *Annalen*, **252**, 308).

Benzoyl-α-diphenylsemicarbazide forms slender needles melting at 156°.

Phenylacetyl-α-diphenylsemicarbazide,

NHPh·CO·NPh·NH·CO·CH₂Ph,
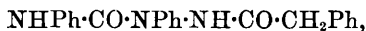
melts at 144°, whilst the *thio*-compound melts at 125—126°.

Cinnamyl-α-diphenylsemicarbazide forms small needles melting at 218—219°.

The acetyl-derivative of benzylphenylhydrazine, a secondary hydr-azine, reacts in a similar manner with phenylcarbimide, *acetylbenzyl-diphenylsemicarbazide,* NHPh·CO·NAc·NPh·C₇H₇, which melts at 145°, being formed.

The hydrazides of bibasic acids do not appear to react with phenyl-carbimide or thiocarbimide.   A. H.

Diazobenzene Perbromide. By E. BAMBERGER (*Ber.*, **27**, 1273—1278).—Diazobenzene perbromide, when shaken with an aqueous solution of sodium hydroxide cooled with ice, yields nitrobenzene, benzenediazoic acid, and small quantities of azobenzene, benzoquinone, orthonitraniline, diphenyl, and carbylamine, together with some quantity of resinous products. The formation of nitrosobenzene from the perbromide is in accordance with its properties as tribromophenylhydrazine, which, when treated with alkalis, should yield nitrosophenylhydroxylamine, and then the latter decomposes according to the equation $OH \cdot NPh \cdot NO = PhNO + NOH$. The greater portion of the nitrosophenylhydroxylamine, however, undergoes molecular change with the formation of benzenediazoic acid. The production of nitrosobenzene is not due to the oxidation of diazobenzene by hypobromite, for only a very minute quantity of nitrosobenzene is formed when an acid diazochloride solution is added to an alkaline bromine solution.

The nitrosobenzene is obtained from the product of the reaction by extraction with ether. The ethereal solution also contains azobenzene, benzoquinone, and very small quantities of nitrobenzene, carbylamine, and diphenyl.

The alkaline liquid, after extraction with ether, contains benzenediazoic acid, orthonitraniline, and probably a salt of nitrosophenylhydroxylamine, since the barium salt, prepared by adding barium chloride to the neutralised solution, when treated with sulphuric acid, yields a small quantity of nitrosobenzene as well as benzenediazoic acid. E. C. R.

Phenylhydroxylamine. By E. BAMBERGER (*Ber.*, **27**, 1548—1557).—The preparation of β-phenylhydroxylamine (this vol., i, 373, 409) from nitrobenzene is a matter of difficulty, since the experimental conditions cause the yield to vary from 0 to 57 per cent.; the physical state of the zinc-dust is of primary importance, and in order to obtain good results it is necessary to test each sample before use, and to modify the conditions accordingly. Phenylhydroxylamine is rapidly oxidised to azoxybenzene on exposure to air, but may be kept for an unlimited time in dry, air-tight vessels; on heating at 100°, it is resolved into azobenzene, aniline, azoxybenzene, paramidophenol, and small quantities of other substances; boiling with water causes a similar decomposition, nitrosobenzene being also formed. Alkalis convert phenylhydroxylamine immediately into nitrobenzene, which then gradually changes into azoxybenzene. The *hydrochloride*, $NHPh \cdot OH, HCl$, is colourless and crystalline.

The *benzylidene-derivative*, $CHPh\!<\!^{O}_{NPh}$, crystallises in lustrous, highly refractive prisms, melts at 108·5—109°, reduces alkaline copper solution on heating, and is resolved into benzaldehyde and paramidophenol (see below) by the action of mineral acids.

Phenylhydroxylamine is readily converted into paramidophenol on treatment with acids, quantities of azobenzene, and other substances, varying according to the experimental conditions, are simultaneously produced.

By the action of nitrous acid on phenylhydroxylamine, the *nitros-amine*, NO·NPh·OH, is formed, and crystallises from light petroleum in long, flat, lustrous needles melting at 58·5—59°; it gives Lieber-mann's reaction, and although certain specimens were stable, others decomposed spontaneously; the cause of this has not yet been de-termined. The yield is 85—90 per cent. of the theoretical. Nitroso-phenylhydroxylamine is immediately converted into nitrosobenzene on heating with acids or water; with acids at ordinary temperatures, a diazo-compound is formed in addition. The nitrosamine reduces alkaline silver solution with difficulty, and alkaline copper solution not at all. The author's previous suggestion that the formation of nitrosobenzene from diazobenzene perbromide is preceded by that of nitrosophenylhydroxylamine (preceding abstract) is confirmed. The *potassium salt*, NO·NPh·OK, crystallises in lustrous plates, resembling naphthalene, and explodes on heating. The *sodium* and *barium salts* are crystalline. The *silver, copper, mercuric*, and *lead salts* are spar-ingly soluble. Nitrosobenzene is formed by the oxidation of phenyl-hydroxylamine; with potassium dichromate and sulphuric acid the yield is 90 per cent. of the theoretical. J. B. T.

Hydrogen Cyanide a Reagent for Symmetrical Oximes, Hydrazones, and Anil-compounds. By W. v. MILLER, J. PLÖCHL, and others (*Ber.*, **27**, 1281—1296).—The authors have already shown that oximes and hydrazones with fatty alkyl-groups take up the elements of hydrogen cyanide, but that those with aromatic groups do not, whereas anil-compounds, both of the fatty and aromatic series, form additive compounds with hydrogen cyanide (Abstr., 1892, 1189). The only exception to this is found in the behaviour of the anhydro compounds of pyruvic acid with amimes, for instance, NPh:CMe·COOH, &c. The authors have now arrived at the follow-ing conclusions:—1. All compounds of the type R·C:N·R' which combine with hydrogen cyanide are symmetrical as regards the nitrogen action, that is, the three bonds of the nitrogen lie in one plane, and stereoisomerides do not exist. 2. If, of two isomeric com-pounds of the above type, one combines with hydrogen cyanide, then the other is not a stereoisomeride, but either a structural isomeride or a polymeride. 3. All simple molecular compounds which do not combine with hydrogen cyanide contain asymmetrical nitrogen. The asymmetry of anil-compounds is determined by the distinct acid or basic properties of the radicle combined with the typical carbon atom. as for example in the anilide of pyruvic acid.

The anilides and toluidides of the glucoses, like other anilides, com-bine with hydrogen cyanide, and are converted into stable nitriles, they must, therefore, have the following constitution, glucose anilide and galactose anilide, OH·CH₂·[CH·OH]₄·CH:NPh, levulose anilide, OH·CH₂·[CH·OH]₃·C(NPh)·CH₂·OH. The nitriles are obtained by allowing the anilides to remain for some time with dilute hydrocyanic acid at the ordinary temperature, or by heating the anilides with aqueous hydrocyanic acid in a sealed tube at 40°. The nitriles de-compose when heated above the melting point with evolution of

hydrogen cyanide, and when warmed with alkalis or water evolve an odour of isonitriles.

Anilidoglucose cyanide crystallises in bunches of needles, and melts at 166—168°; *toluidoglucose cyanide* melts at 128°; *anilidogalactose cyanide* melts at 138°; *toluidogalactose cyanide* melts at 145—146°; *anilidolevulose cyanide* melts at 131°.

When the above nitriles are allowed to remain for some time with fuming hydrochloric acid, they yield strongly acid, syrupy compounds which reduce silver and copper solutions. Crystalline phenylhydrazides are obtained when the nitriles are hydrolysed by allowing them to remain with very dilute alkali. and, after acidifying the solution with acetic acid, warming with phenylhydrazine. The hydrazides, when treated with concentrated sulphuric acid and ferric chloride, give a reddish-violet coloration.

Anilidoglucosecarboxylic acid phenylhydrazide crystallises in long interlacing needles, and melts at 210°; *toluidoglucosecarboxylic acid phenylhydrazide* crystallises in plates, and melts at 211—212°; *anilidogalactosecarboxylic acid phenylhydrazide* melts at 203°; *toluidogalactosecarboxylic acid phenylhydrazide* melts at 206°.

Glucoseoxime does not combine with hydrogen cyanide either at the ordinary temperature or when warmed at 40°. The hydrazone and osazone also do not combine with hydrogen cyanide.

Aldoleanilide, $OH \cdot CHMe \cdot CH_2 \cdot CH \colon NPh$, is obtained by adding aniline to aldole in ethereal solution. It melts at 73—75°. The nitrile is best prepared by adding an ethereal solution of aldole to a mixture of aniline and hydrogen cyanide dissolved in ether. The product, *α-phenylamido-γ-hydroxyvaleronitrile*,

$$OH \cdot CHMe \cdot CH_2 \cdot CH(CN) \cdot NHPh,$$
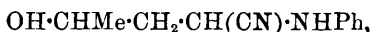
is a viscid, greenish-yellow oil. When hydrolysed with hydrochloric acid, it yields the *lactone*, $NHPh \cdot CH {<} {COO \atop CH_2 \cdot} {>} CHMe$, which crystallises in needles, and melts and decomposes at 59°. α-Phenylamido-γ-hydroxyvaleric acid is obtained by treating the lactone with sodium hydroxide; it crystallises in small nodules, and melts and decomposes at 143°.

The phenylhydrazide of aldole is prepared in a similar way to the anilide; it is a reddish oil. The *nitrile* is a viscid, greenish oil, which, when rubbed with concentrated hydrochloric acid, yields the *lactone*, $N_2H_2Ph \cdot CH {<} {COO \atop CH_2 \cdot} {>} CHMe$, which crystallises in lustrous leaflets, and melts at 113°.　　　　　　　　　　　　　　E. C. R.

Salts of Phenylhydrazine. By H. J. F. DE VRIES (*Ber.*, **27**, 1521—1522).—*Phenylhydrazine formate* is a colourless, crystalline mass, which becomes yellowish-brown in the air; it is very readily soluble in water, and melts at 89—90°. *Phenylhydrazine lactate* melts at 102—103°. Formylphenylhydrazine, which is obtained instead of phenylhydrazine formate when an excess of formic acid is mixed with phenylhydrazine, melts at 140°, and not at 145°, as stated by other investigators.　　　　　　　　　　　　　　A. H.

Dihydroxamic acids. By W. Lossen (*Ber.*, **27**, 1481).—The action of alkalis on dihydroxamic acids, which Hantzsch (this vol., i, 364) thinks he has studied for the first time in the case of benzacethydroxamic acid, was described long ago by the author.

C. F. B.

Nitrogen Halogen Compounds. By F. Lengfeld and J. Stieglitz (*Amer. Chem. J.*, **16**, 370—372; compare Abstr., 1893, i, 310, 631).—*Methylic paranitrophenylcarbamate*, $NO_2 \cdot C_6H_4 \cdot NH \cdot COOMe$, results, together with paranitraniline, from the reaction between paranitrobenzobromamide and sodium methoxide. It forms light, yellow crystals, melts at 176°, and volatilises when carefully heated, otherwise it explodes. It is identical with the carbamate synthetised from paranitraniline and methylic chlorocarbonate. The paranitraniline obtained as a co-product in the first process obviously results from the decomposition of the carbamate.

Methylic methylcarbamate, $NHMe \cdot COOMe$, results in a similar manner from the reaction between acetobromamide and sodium methoxide, and is also identical with the synthetical product. It is a colourless oil of peculiar odour, and boils at 55—60° under a pressure of 25 mm., and at 158° under the ordinary pressure.

Jn. W.

Blue Lakes derived from Dibromogallanilide; Blue Reactions of Polyphenols. By P. Cazeneuve (*Compt. rend.*, **118**, 1046—1048). —When ammonia, or potassium or sodium hydroxide, is added carefully to a solution of dibromogallanilide, a deep indigo-blue compound is formed which is readily decomposed by excess of air or an excess of alkali. The blue colour becomes green, and then yellow. Under the same conditions calcium or barium hydroxide yields a white precipitate, which becomes blue on contact with air, the blue compound remaining unaltered when left in contact with water; a feeble acid, such as carbonic acid, decomposes the blue substance, and sets free a red acid which is decomposed by strong acids. The calcium and barium lakes alter in contact with air, but the zinc compound is more stable. It is prepared by adding zinc acetate solution to a dilute alcoholic solution of dibromogallanilide in the proportion of 2 mols. of the former to one of the latter, and is at first white, but becomes blue when exposed to air. The blue compound can be dried over sulphuric acid without undergoing appreciable alteration; it has the composition $NHPh \cdot CO \cdot C_6Br_2O_2(O_2Zn) \cdot OH$.

It is noteworthy that all polyphenols derived from pyrogallol yield blue compounds. Gallic acid, dibromogallic acid, methylic dibromogallate, and the other ethereal salts, and the gallanilide, yield blue compounds which remain unaltered in contact with water for a long time. Purpurogallin and pyrogalloquinone yield fugitive blue compounds with ammonia.

C. H. B.

Iodoso- and Iodoxy-compounds. By C. Willgerodt (*J. pr. Chem.*, [2], **49**, 466—482).—In the first portion of this paper the author replies to the criticisms of V. Meyer (Abstr., 1893, i, 713).

By chlorinating orthiodobenzoic acid in chloroform, yellow prisms, which melt and decompose at 115—123°, and are unstable in

air, are obtained. The composition of this compound agrees with the formula $C_6H_4<^{CO}_{ICl}>O$. When the chlorination is conducted in glacial acetic acid, a different chlorine derivative is obtained; this melts and partially decomposes at 95°. Iodosobenzoic acid (ortho-hydroxyiodobenzoate) has been prepared from the first-mentioned chloride by Meyer (Abstr., 1893, i, 507); by passing hydrogen chloride through a glacial acetic acid solution of the acid, prisms are formed which are apparently identical with the second chloride referred to above; they melt and decompose at 85—90°; water decomposes them with formation of iodosobenzoic acid. The nitrate, $C_6H_4<^{CO——}_{I(NO_3)}>O$, was prepared by heating a glacial acetic acid solution of iodosobenzoic acid with fuming nitric acid; it is decomposed by water into nitric acid and iodosobenzoic acid.

<div style="text-align:right">A. G. B.</div>

Preparation of the Peroxides of the Acid Radicles. By H. v. PECHMANN and L. VANINO (*Ber.*, **27**, 1510—1512).—Benzoic peroxide can be readily prepared by shaking a 10 per cent. solution of hydrogen peroxide with aqueous soda and benzoic chloride, a yield of 70 per cent. being obtained. This modified method may also be applied to the preparation of the peroxides derived from the bibasic acids which Brodie was unable to obtain, but the yields are not so satisfactory.

Phthalic peroxide, $C_8H_4O_4$, is best prepared by shaking a solution of sodium peroxide in aqueous sodium acetate with phthalic chloride. It is a crystalline powder, insoluble in the ordinary solvents. It melts when carefully heated at 133·5°, but explodes when rapidly heated or when struck. The substance may be analysed by heating it with a standard solution of stannous chloride. It possesses all the characteristic properties of the acid peroxides, liberates iodine from potassium iodide, decolorises indigo, &c.

<div style="text-align:right">A. H.</div>

Bismuth Salts. By B. FISCHER and E. GRÜTZNER (*Arch. Pharm.*, **231**, 680—686).—After reviewing the past work on "bismuthum salicylicum," all of which shows the variability of the commercial product, the authors recommend the following method of obtaining a basic bismuth salicylate of constant composition, namely $BiO \cdot C_7H_5O_5$. Crystallised bismuth nitrate is dissolved in about four times its weight of dilute acetic acid (concentration not stated), the solution is diluted with about 40 times its weight of water, and the bismuth precipitated as hydroxide by the addition of ammonia. The precipitate is washed and mixed with a molecular proportion of salicylic acid. After a heating of some duration on the water bath, a magma of crystals of basic bismuth salicylate is formed. This is drained and dried, first on a porous tile and then in the air bath at 70—75°. The preparation is a dry, electrical, white powder, consisting of microscopic prisms, reddening moistened blue litmus only after a time. No salicylic acid can be detected in cold water in which the powder has been shaken.

Bismuth subgallate (dermatol), $C_6H_2(OH)_3 \cdot COO \cdot Bi(OH)_2$, may be prepared by a similar method from bismuth hydroxide and gallic acid. It is a sulphur-yellow powder, which does not part with gallic acid either to alcohol or to hot water. A. G. B.

Methylic Parahydroxybenzoate. By C. H. v. HOESSLE (*J. pr. Chem.*, [2], **49**, 501—502).—Ladenburg and Fitz prepared this compound, but they were dealing with an impure product when they determined its constants (*Annalen*, **141**, 250). It crystallises in monoclinic, stellate needles, melts at 131°, and boils at 270—280°. Its *acetyl*-derivative crystallises in slender, felted needles, dissolves in alcohol, and melts at 85°. The *benzoyl*-derivative crystallises in slender, white needles, and melts at 135°; it dissolves in hot alcohol, but not in water. A. G. B.

Reduction Product of Orthosulphobenzoic Chloride. By W. JONES (*Amer. Chem. J.*, **16**, 366—369).—Orthosulphobenzoic chloride is reduced by aqueous potassium hydrosulphide, with development of much heat, to the corresponding sulphonephthalide. This separates when the well-diluted product is acidified with hydrochloric acid. The same compound is obtained when zinc and dilute hydrochloric acid are substituted for the hydrosulphide. The product is dissolved in dilute caustic alkali, and isolated as before.

Sulphonephthalide, $C_6H_4 {<}{CH_2 \atop SO_2}{>}O$, forms colourless crystals, and melts and decomposes at 287—289°. It reduces permanganate, and is oxidised by concentrated nitric acid to orthosulphobenzoic acid. It forms a fluorescent compound with resorcinol, but oxidation probably occurs at an intermediate stage. The constitution of the phthalide is probably that represented by the above formula, but is still under investigation. JN. W.

Indoxazenes. By A. HEIDENREICH (*Ber.*, **27**, 1452—1456; compare Cathcart and V. Meyer, Abstr., 1893, i, 94).—*Orthobromophenyltolyl ketone* is prepared by the action of aluminium chloride on orthobromobenzoic chloride and toluene, and crystallises from alcohol in long needles melting at 92—93°. The *oxime* is crystalline, and melts at 138—140°. *Tolylindoxazene*, $\overset{C_6H_4}{\underset{O \cdot N}{}} {>} C \cdot C_6H_4Me$, is formed by heating the preceding compound with aqueous alkali or sodium ethoxide, and crystallises in long, colourless needles; it boils at 344—346°, and melts at 81—82°. The *dinitro*-derivative is crystalline, and melts at 187—188°. *Dibromobenzophenone*, prepared from orthobromobenzoic chloride, bromobenzene, and aluminium chloride, crystallises from alcohol, and melts at 51—52°. The *oxime* is crystalline, and melts at 140—142°. *Parabromophenylindoxazene*, $\overset{C_6H_4}{\underset{O \cdot N}{}} {>} C \cdot C_6H_4Br$, crystallises in long needles, and melts at 132—133°. *Ethoxyorthobromobenzophenone* is prepared in a similar manner to the preceding ketones, and forms greenish crystals melting at 79°. The *oxime* melts at

161—163°. *Ethoxyphenylindoxazene,* $\begin{smallmatrix} C_6H_4 \\ | \\ O \cdot N \end{smallmatrix} {>} C \cdot C_6H_4 \cdot OEt$, is deposited from alcohol in brownish crystals melting at 59—61°. *Methoxyortho-bromobenzophenone* is colourless and crystalline, and melts at 95—95·5°. The *oxime* could not be obtained in a state of purity. *Methoxyphenyl-indoxazene,* $\begin{smallmatrix} C_6H_4 \\ | \\ O \cdot N \end{smallmatrix} {>} C \cdot C_6H_4 \cdot OMe$, is deposited from alcohol in slender, lustrous crystals melting at 100—101°. Attempts to extend this reaction to the thiophen and naphthalene series were unsuccessful, it was not even possible to prepare the corresponding ketones.

J. B. T.

Benzidinethiocarbimides. By M. JAFFÉ (*Ber.*, **27**, 1557—1561). —*Diphenylenedithiocarbimide*, $C_{12}H_8(NCS)$, is prepared by the interaction of benzidine and thiocarbonyl chloride at 180°, and crystallises from benzene in highly refractive, colourless needles melting at 203°. By the action of ammonia, two compounds are formed, the one, $NH {<} \begin{smallmatrix} CS \cdot NH \cdot C_6H_4 \\ | \\ CS \cdot NH \cdot C_6H_4 \end{smallmatrix}$, crystallises from benzene in lustrous plates, which remain unmelted at 300°; the second is *diphenylenedithiocarbamide*, $C_{12}H_8(NH \cdot CS \cdot NH_2)_2$; this is obtained pure by the action of alcoholic ammonia on the imide, and is only soluble in nitrobenzene. *Diphenyl-enediisopropylthiocarbamide* is prepared by heating benzidinethiocarbimide and isopropylamine in benzene solution; it is a colourless, amorphous powder, which is unmelted at 300°; a second modification, crystallising in needles, is deposited from the mother liquor, and melts at 170°. *Diphenylenediamyldithiocarbamide* is prepared in a similar manner to the preceding compound, which it closely resembles, the mother liquor on standing deposits *diphenyleneamyldithiocarbamide*, $C_5H_{11} \cdot N {<} \begin{smallmatrix} CS \cdot NH \cdot C_6H_4 \\ | \\ CS \cdot NH \cdot C_6H_4 \end{smallmatrix}$, which is crystalline, and melts at about 148°.

Diphenylenediorthotolyldithiocarbamide, prepared from orthotoluidine and benzidinethiocarbimide is amorphous, is not melted at 300°, and on repeatedly heating in benzene solution becomes insoluble. Diphenyl-enediphenyldithiocarbamide is already known, and, like the preceding compound, exists in a colloïdal form; by the action of phenylhydrazine the *thiosemicarbazide*, $\begin{smallmatrix} C_6H_4 \cdot NH \cdot CS \cdot NPh \\ | \\ C_6H_4 \cdot NH \cdot CS \cdot NH \end{smallmatrix}$, together with the *disemi-carbazide*, $C_{26}H_{24}N_6S_2$, are formed; the former crystallises from benzene in thin plates, and melts and decomposes at 220—230°, the latter is amorphous, insoluble, and does not melt. *Unsymmetrical diphenyl-enetetraisobutyldithiocarbamide*, $C_{12}H_8[NH \cdot CS \cdot N(C_4H_9)_2]_2$, from benzid-inedithiocarbamide and diisobutylamine, crystallises from alcohol in colourless needles melting at 185°. The corresponding *amyl derivative* crystallises in needles melting at 162.° A second modification melting at 123° was also obtained. *Diphenylenedimethyldiphenyldithiocarb-amide*, from the thiocarbamide and methylaniline, is crystalline. *Diphenylenedipiperidyldithiocarbamide* crystallises from alcohol in slender, colourless needles, melts at 214—215°, and by prolonged heat-

ing with benzene is converted into an insoluble modification, which does not melt. J. B. T.

Tetramethyldiamidobenzhydrol. By H. WEIL (*Ber.*, **27**, 1403 —1409).—The reactions described below resemble those of ketones and aldehydes, and lead to the conclusion that tetramethyldiamidobenzhydrol has not the constitution $OH \cdot CH(C_6H_4 \cdot NMe_2)_2$, but $NMe_2 \cdot C_6H_4 \cdot CO \cdot C_6H_6 \cdot NMe_2$, or, possibly,

$$NMe_2 \cdot C_6H_4 \cdot C(OH) : C_6H_4 : NHMe_2,$$
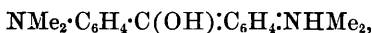
in which one of the benzene rings is dihydrogenised. In the case of the action of sodium hydrogen sulphite or of hydrogen cyanide the CO group may be supposed to first react as usual, an interchange of OH and H then taking place, with subsequent loss of H_2O and formation of the substance actually obtained.

Tetramethyldiamidobenzhydrol yields with hydroxylamine the *oxime*, $NMe_2 \cdot C_6H_4 \cdot C(NOH) \cdot C_6H_6 \cdot NMe_2$, melting and decomposing at 154°. With sodium hydrogen sulphite it yields the sodium salt of a *sulphonic acid*, $SO_3H \cdot CH(C_6H_4 \cdot NMe_2)_2$, which, when heated, evolves sulphurous anhydride at 120—130°; the acid can also be obtained by the action of sulphurous anhydride on the hydrol in alcoholic solution. With hydrogen cyanide, it yields a *nitrile*, $CN \cdot CH(C_6H_4 \cdot NMe_2)_2$, which melts at 124°, and behaves like a leucobase, being capable of oxidation to a green-colouring matter. The nitrile can be converted by hydrolysis into a *carboxylic acid*, $COOH \cdot CH(C_6H_4 \cdot NMe_2)_2$, which greatly resembles the sulphonic acid in physical properties. When the hydrol is boiled with a concentrated solution of ammonium acetate carefully kept feebly alkaline with ammonia, a compound $NH[CH(C_6H_4 \cdot NMe_2)_2]_2$, melting at 185°, is formed. C. F. B.

Ketotetrahydronaphthalene. By E. BAMBERGER and A. VOSS (*Ber.*, **27**, 1547—1548).—The preparation of ketotetrahydronaphthalene, $C_6H_4 {<}{{CH_2 \cdot CH_2} \atop {CH_2 \cdot CO}}$, from tetrahydronaphthalene chlorhydrin,

$$C_6H_4 {<}{{CH_2 \cdot CHCl} \atop {CH_2 \cdot CH \cdot OH}},$$
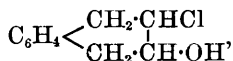
by distillation with magnesium carbonate or quinoline has been previously described (Abstr., 1893, 1591). The yield is small. The ketone is a colourless, highly refractive oil, which solidifies in a freezing mixture, melts at 18°, and boils at 138° under 16 mm. pressure; under ordinary pressure, the boiling point is 130—140°, and a portion is decomposed into naphthalene and water. The sodium hydrogen sulphite derivative crystallises in colourless, lustrous plates. The *phenylhydrazone*, $C_6H_4 {<}{{CH_2 \cdot CH_2} \atop {CH_2 \cdot C \cdot N_2HPh}}$, is deposited in colourless, lustrous crystals which melt at 107·5—108°; it rapidly decomposes on exposure to sunlight, and gives Bülow's re-

action.   The *oxime*, $C_6H_4{<}{\displaystyle{CH_2{\cdot}CH_2 \atop CH_2{\cdot}C{:}NOH}}$, crystallises from dilute alcohol in silky, lustrous, stellate needles melting at 87·5—88°.

<div align="right">J. B. T.</div>

Derivatives of Naphthyl Ethyl Ether. By P. HEERMANN (*J. pr. Chem.* [2], **49**, 504).—A reply to Duisberg (this vol., i, 336).

β-Anthraquinone. By K. LAGODZINSKI (*Ber.*, **27**, 1438—1439). —When 2-hydroxyanthracene is heated in alcoholic solution with sodium nitrite and zinc chloride, it is converted into a salt of *nitrosohydroxyanthracene*, which in the free state forms a brown mass. On treatment with stannous chloride and hydrochloric acid this is reduced to *amidohydroxyanthracene*, the hydrochloride of which crystallises in slender, matted needles, which do not change in the air. When this substance is oxidised by means of chromic acid, a new anthraquinone is formed which crystallises from a mixture of benzene and light petroleum in beautiful, orange-yellow needles, and is almost insoluble in water. It melts and decomposes at about 180°. With phenylenediamine it reacts with great readiness, forming an azine, which exhibits the usual reactions with acids. It has not yet been determined whether the compound is a 1 : 2- or a 2 : 3-quinone.

<div align="right">A. H.</div>

Truxene. By C. LIEBERMANN (*Ber.*, **27**, 1416—1418).—A polemical paper in relation to the author's work (with Bergami) (*Ber.*, **22**, 782; **23**, 317) and that of Kipping (Proc., 1892, 107; Trans., 1894, 269).

The Truxillic acids. By H. LANGE (*Ber.*, **27**, 1410—1415).— γ-Truxillic acid yields derivatives with toluidine which are analogous to those obtained with aniline (Abstr., 1893, i, 418). *γ-Truxillotoluidic acid*, $HOOC{\cdot}C_{16}H_{14}{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$, forms white, needle-shaped crystals, melts at 268°, and is less soluble in aqueous soda than γ-truxillic acid itself. The *barium* salt is sparingly soluble in water. *γ-Truxilloditoluidide*, $C_{16}H_{14}(CO{\cdot}NH{\cdot}C_6H_4Me)_2$, is obtained by the use of an excess of toluidine, and melts at 289°.

All the three isomeric truxillic acids react with phenylhydrazine to form hydrazides. The α-acid only forms one compound, *α-truxillodiphenylhydrazide*, $C_{16}H_{14}(CO{\cdot}NH{\cdot}NHPh)_2$, which is insoluble in the usual reagents and in alkalis, but crystallises from phenol or acetin in white needles melting at 320°.

γ-Truxillodiphenylhydrazide is a similar substance, and melts at 305°. When truxillic anhydride is heated with phenylhydrazine, however, *γ-truxillophenylhydrazide*, $C_{16}H_{14}(CO)_2N{\cdot}NHPh$, is obtained. This compound is also sparingly soluble in most solvents, and separates from acetic acid in white prisms melting at 249°. It corresponds with the hydrazide obtained from the β-acid, and marks the distinction between these two and the α-acid, which is incapable of forming an anhydride. γ-Truxillic acid reacts with sulphuric acid in a different manner from the α- and β-acids (Abstr., 1889, 698). No truxillodisulphonic acid or truxone is produced, but the acid is converted into *dicinnamenedisulphonic acid*, $C_{16}H_{14}(SO_3H)_2$.

A number of acid salts of the α- and γ-acids have also been prepared, the bibasic character of these acids being thus further confirmed. *Hydrogen silver α-truxillate*, $COOH \cdot C_{16}H_{14} \cdot COOAg$, is almost insoluble in water, readily soluble in ammonia. *Hydrogen methylic α-truxillate* is prepared from the hydrogen silver salt. It forms small, white needles, and melts at 195°. *Silver methylic α-truxillate* is a white precipitate. *Hydrogen silver γ-truxillate* resembles the corresponding α-salt. The *hydrogen methylic* salt of the γ-acid melts at 180°, and the *silver methylic* salt is a white precipitate.

The γ-acid does not yield a fluoresceïn, and differs in this respect from the β-acid.　　　　　　　　　　　　　　　　　　　　A. H.

Oxidation Products of Carvole. By O. WALLACH (*Ber.*, **27**, 1495—1496; compare Abstr., 1893, i, 596). A paper has recently been published by Best (this vol., i, 361) dealing with the products of oxidation of carvole, which have previously been described by the author. These products are still under investigation. The acid of higher melting point when pure crystallises well, and melts at 192·5° (previously stated as 185°) with loss of water. It has the composition $C_8H_{12}O_5$, and yield a white *silver* salt, $C_8H_{11}O_5Ag$. When this acid is distilled under diminished pressure, it is converted into a neutral substance of the formula $C_8H_{10}O_4$ (previously stated to be $C_{10}H_{12}O_5$), melting at 129°. The acid described as melting at about 100°, crystallises well when pure, and melts at 94—95°. It is isomeric with terpenylic acid, $C_8H_{12}O_4$, is a well marked bibasic acid, and forms a *silver* salt, $C_8H_{10}O_4Ag_2$.　　　　　　　　　　　　　　　　　　A. H.

Stereoisomerism in the Camphor Group. By L. BOUVEAULT (*Bull. Soc. Chim.*, [3], **11**, 134—144; compare Abstr., 1893, i, 523).—The author has already described a saturated hydrocarbon isomeric with hydrocamphene, obtained by the action of sodium on boiling pinene hydrochloride (*loc. cit.*). In order to explain the relation between these two compounds, an hypothesis is developed embodying an application to the terpene series of v. Baeyer's views regarding the cistrans-isomerism of hexamethylene derivatives (compare A. v. Baeyer, this vol., i, 92). The liquid hydrocarbon is now called *cis-hydrocamphene*, the previously known, solid modification receiving the name *cistrans-hydrocamphene*. To these isomerides the author assigns

the constitution $CMe{\Large\langle}\genfrac{}{}{0pt}{}{CHMe \cdot CH_2}{\genfrac{}{}{0pt}{}{-CH_2 \cdot CH_2}{CH_2\text{---}CH_2}}{\Large\rangle}CH$, thence deducing the following constitutional formula:

$$CMe{\Large\langle}\genfrac{}{}{0pt}{}{CHMe \cdot CH_2}{\genfrac{}{}{0pt}{}{-CH\text{:}CH-}{CH_2\text{---}CH_2}}{\Large\rangle}CH \text{ ;}$$
Camphene.

$$CMe{\Large\langle}\genfrac{}{}{0pt}{}{CHMe \cdot CH_2}{\genfrac{}{}{0pt}{}{-CH_2 \cdot CH=}{CH_2\text{---}CH_2}}{\Large\rangle}C \text{ ;}$$
Pinene.

$$CMe{\Large\langle}\genfrac{}{}{0pt}{}{CHMe \cdot CH_2}{\genfrac{}{}{0pt}{}{-CO \cdot CH_2-}{CH_2\text{---}CH_2}}{\Large\rangle}CH \text{ (compare Bredt, this vol., i, 141) ;}$$
Camphor.

$$COOH \cdot CH \underset{CH_2CHMe}{\overset{CH_2 - CH_2}{\diagdown}} CMe \cdot COOH.$$
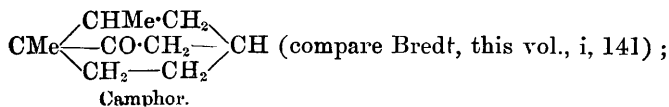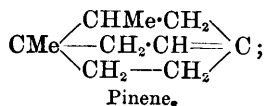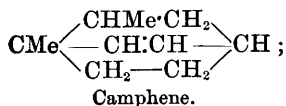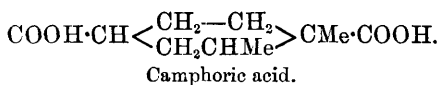
Camphoric acid.

According to the views adopted by the author, camphoric acid could exist in four modifications; whilst camphor, camphene, hydrocamphene, and pinene hydrochloride might each be expected to occur in two stereoisomeric forms.   M. O. F.

Optical Isomerism of Closed Chain Compounds. By L. BOUVEAULT (*Bull. Soc. Chim.*, [3], **11**, 144—147).—A further discussion of cistrans-isomerism in the terpene series.   M. O. F.

Bredt's Camphor Formula. By O. ASCHAN (*Ber.*, **27**, 1439—1446).—The author considers Bredt's formula for camphor (this vol., i, 141) the best hitherto suggested, but it fails to explain the non-formation of an unsaturated acid or anhydride by the elimination of hydrogen bromide from bromocamphoric anhydride; that the bromine in this compound is linked to a tertiary carbon atom as in bromo-benzene is irrelevant, since the anhydride does not contain a benzene linkage. The readiness with which hydrogen bromide is eliminated from the two α-bromohexahydroterephthalic acids, α-bromohexa-hydrobenzoic acid, α-bromohexahydroparatoluic acid, and from α-bromethylcyclopentanecarboxylic acid, would suggest that bromo-camphoric anhydride, which, like this last acid, contains the group $CH_2 \cdot CBr \cdot CO$, should behave in a similar manner. Since the bromine atom is readily eliminated, we must conclude that it is probably linked to a secondary carbon atom which is itself linked either to two tertiary carbon atoms, or to one of these and to a carboxyl group. Similar arguments are applied to bromocamphor; according to Bredt this contains the group $CH \cdot CHBr \cdot CO$, but in this case, too, hydrogen bromide is not eliminated, as from analogy would be expected; the compound remains unaltered by prolonged boiling with aniline or quinoline.

Bromocamphocarboxylic acid is readily prepared by the action of bromine on camphocarboxylic acid in glacial acetic acid solution, and melts at 112—113°; the substance obtained by Silva's method is impure, and melts at 109—110°. Bromocamphor was prepared from the preceding compound by the action of alcoholic potash at the ordinary temperature.   J. B. T.

Formation of Camphorquinone by the Oxidation of Camphocarboxylic acid with Potassium Permanganate. By O. ASCHAN (*Ber.*, **27**, 1446—1449).—Bromocamphocarboxylic acid and camphocarboxylic acid are stable towards potassium permanganate in alkaline solution at ordinary temperatures; the former acid is only slowly decomposed on boiling, the latter, at 60—70°, yields camphor-quinone, camphoric anhydride, and camphoric acid. The yield of quinone is 0·25 per cent. of the acid employed. The camphoric anhydride is almost certainly formed from the quinone, and the yield varies according to the experimental conditions. The preparation of

camphoric acid by the oxidation of camphor with nitric acid is probably preceded by the formation of camphorquinone and camphoric anhydride. These results are not in agreement with the camphor formulæ, which, like that of Collie (Abstr., 1892, 864), represent the production of camphoric acid from camphor as involving molecular rearrangement of the ring system. J. B. T.

Galbanum Resin. By A. CONRADY (*Arch. Pharm.*, **232**, 98—130). —This substance has been submitted to a careful examination, and is found to consist of (1) an ethereal oil, 9·5 per cent.; (2) a resin soluble in alcohol, 63·5 per cent.; (3) impurities and gum, 27·0 per cent. The pure resin, obtained from the commercial product by extraction with alcohol and subsequent treatment with sodium salicylate, contains (1) combined umbelliferone, 20 per cent.; (2) galbaresinotannol, 50 per cent.; (3) free umbelliferone, 0·25 per cent. A solution of the pure resin in cold caustic potash shows a blue fluorescence, indicating the formation of umbelliferone; on heating the solution, umbellic acid is formed. Since umbelliferone is unattacked by sulphuric acid, the hydrolysis of the resin is best effected by that reagent, about 20 per cent. of umbelliferone being obtained in this way; the other product of hydrolysis is *galbaresinotannol*, $C_{18}H_{30}O_3$, from which *barium*, *acetyl*, and *benzoyl* derivatives were obtained, the two latter melting at 61° and 73° respectively. Galbaresinotannol, therefore, contains an hydroxyl group, and the pure resin is most probably a galbaresinotannylic salt of umbelliferone. Distillation of the resin alcohol with phosphoric anhydride gives rise to a hydrocarbon of the formula $C_{15}H_{20}$, and oxidation with nitric acid (sp. gr. = 1·27) leads to the formation of camphoric and camphoronic acids. The ethereal oil of commercial galbanum oil undergoes decomposition in a current of steam, with formation of isovaleric acid and a terpene, probably associated with a sesquiterpene (compare Wallach, Abstr., 1887, 596). M. O. F.

Peru Balsam. By H. TROG (*Arch. Pharm.*, **232**, 70—98).—By suitable treatment with carbon bisulphide, ether, and a dilute solution of caustic soda (0·5 per cent.), Peru balsam is divided into two constituents, an oil and a resin, both of which have been carefully examined.

The author summarises his results as follows. The liquid portion of Peru balsam, known as cinnameïn to earlier investigators, consists chiefly of benzylic benzoate with a small quantity of benzylic cinnamate; ethylic and phenylpropylic cinnamates, benzylic alcohol, and benzoic acid were not detected, but cinnamic acid and vanillin are present in very small quantities. The resin, when hydrolysed, yields cinnamic acid and a small quantity of benzoic acid, together with *peruresinotannol*, a resin alcohol of the formula $C_{18}H_{20}O_5$, forming a pale brown, odourless powder, which shrinks and gradually decomposes when heated. From peruresinotannol were obtained a *potassium salt*, and *acetyl*, *benzoyl*, and *cinnamyl* derivatives. It can be brominated, and is oxidised by concentrated nitric acid to oxalic and picric acids (compare Lüdy, Abstr., 1893, i, 480).

The bark of *Myroxylon Pereirae* contains very small quantities of phloroglucinol, tannic acid, phlobaphen, and wax, together with an unsaponifiable resin, but it is free from all the constituents of the balsam. Since the uninjured bark contains neither secreting vessels nor secretions, Peru balsam must be regarded, similarly to gum benzoïn, as a pathological product, its formation being probably due to an accumulation of tannin, caused by bruising the bark.

<div align="right">M. O. F.</div>

Flores Koso. By M. LEICHSENRING (*Arch. Pharm.*, **232**, 50—65). —From this drug, the author has isolated two individual substances, in addition to kosin, which has hitherto been regarded as the principle to which the koso bloom owes its vermifugal action. Kosin, $C_{23}H_{30}O_7$ (compare Flückiger and Buri, this Journal, 1875, 468), crystallises from boiling alcohol in tufts of long, pale yellow needles, which melt at 148°. It is uncertain whether kosin contains hydroxyl groups, but, when it is heated at 150—170° with sulphuric acid in a closed tube, two molecular proportions of isobutyric acid are eliminated; if hydrochloric acid is employed, an amorphous, red substance is formed, very similar to that obtained in association with isobutyric acid by the decomposition of filicic and pannic acids. Kosin is almost insoluble in weak alkalis, and is non-poisonous.

Protokosin, $C_{29}H_{36}O_9$, is isolated from the ethereal extract of the drug in the form of long, colourless, shining needles, melting at 176°. It is insoluble in water, and but slightly soluble in cold alcohol, dissolving readily in ether; when heated alone or with sulphuric acid, an odour of isobutyric acid becomes perceptible. Protokosin is without physiological action, and the poisonous character of the original drug has now been traced to the presence of *kosotoxin*, $C_{26}H_{34}O_{10}$, a pale yellow powder, which melts at 80°. It is insoluble in water, but dissolves readily in alcohol, ether, aqueous alkalis, and alkali carbonates. It has no action on litmus, and closely resembles kosin in properties, giving rise to isobutyric acid when heated alone or with sulphuric acid. A solution of kosotoxin in potash reduces copper sulphate when boiled, an ammoniacal solution causing silver nitrate to deposit a metallic mirror. Ferric chloride develops, in an alcoholic solution, a deep, brownish-red coloration, this being immediately destroyed by hydrochloric acid. In distinction from kosin, kosotoxin yields two molecular proportions of isobutyric acid when heated with caustic potash, and, if boiled for 20 minutes with a 5 per cent. solution of barium hydroxide, gives rise to the formation of kosin.

<div align="right">M. O. F.</div>

Pyridine Series. By S. RUHEMANN (*Ber.*, **27**, 1266—1273; see also *Ber.*, **27**, 1099).—*Phenylhydrazoneoxalhydroxyfumaric acid.* $NHPh:C(COOH)\cdot C(COOH):C(OH)\cdot COOH$, is obtained by heating the hydrazone, $C_{12}H_9ClN_4O_3$, obtained from chlorodiketohydroxyiso-nicotinamide, with potassium hydroxide. It is separated by converting into the *silver salt*, $C_{12}H_7N_2O_7Ag_3$, and treating the latter with hydrogen sulphide. It crystallises in slender, yellow needles, and melts at 130°, gas being evolved. The *methylic salt* is obtained by warming the silver salt with methylic iodide, and, when treated with

concentrated ammonia, is converted into the *amide* of *phenylhydroxy-pyridazonedicarboxylic acid,* $\begin{array}{c}\text{NPh·N}\overline{\quad\quad}\text{C·CONH}_2\\[2pt]\text{CO·C(OH):C·CONH}_2\end{array}$. This crystallises in colourless needles and melts at 237—238°.

When citrazinamide is heated with a solution of potassium hydroxide in a sealed tube at 150°, it is converted into aconitic acid (m. p. 187°). A decomposition analogous to that obtained by the action of potassium hydroxide on the pyridine compounds derived from citrazinamide.

The author has already described dihydroxypyridines derived from the ethereal salts of homologues of glutaconic acid (Trans., 1893, 874). These compounds give a yellow coloration with ferric chloride. The author has obtained, from their mother liquors, isomeric compounds, which yield a violet coloration with ferric chloride.

The compound, obtained by the action of ammonia on methylic glutaconate, which melts at 190—191°, yields a dibromo-derivative, which has the constitution $\text{CH}\!<\!\!\begin{array}{c}\text{CMe·C(OH)}\\[2pt]\text{CBr}_2\!\!-\!\!\text{CO}\end{array}\!\!>\!\!\text{N}$, and not that previously assigned to it, for, by the action of phenylhydrazine, it yields the *phenylhydrazone* of *methyldiketohydroxypyridine*, which crystallises in yellowish-red needles and decomposes at 240°.

Phenylmethylpyridazonecarboxylic acid, $\text{CO}\!<\!\!\begin{array}{c}\text{NPh}-\text{N}\\[2pt]\text{CMe:CH}\end{array}\!\!>\!\!\text{C·COOH}$, is obtained by boiling the preceding hydrazone with potassium hydroxide in a reflux apparatus. It crystallises in colourless needles, melts at 216°, and is a strong acid.   E. C. R.

Crystalline form of β-Pipecoline Tartrate. By A. LADENBURG (*Ber.*, **27**, 1409—1410).—The data given in a previous communication (this vol., i, 208) apply to *d*α-pipecoline dextrotartrate. The corresponding data for *l*β-pipecoline dextrotartrate are as follows. The crystals are strongly developed, parallel to the vertical axis, and belong to the hemihedral division of the rhombic system. Axial ratio = 0·28801 : 1 : 0·30255.   A. H.

Derivatives of Picolinic acid and their Conversion into α-Amidopyridine. By H. MEYER (*Monatsh.*, **15**, 164—182).—The ethylic salts of the pyridinemonocarboxylic acids cannot be prepared in the usual ways, betaïnes being formed instead. The author has now succeeded in preparing *ethylic picolinate* by heating an intimate mixture of dry potassium ethylic sulphate and potassium picolinate, moistened with absolute alcohol, for 7—9 hours at 150° in an autoclave. In this reaction, ethylpyridylium hydroxide is also produced. Ethylic picolinate forms a colourless oil of faint aldehydic odour and burning taste. It boils at 240—241° (corr.), and remains liquid at −17°, but at −65° solidifies to colourless crystals melting at 0—2°. It is volatile in steam, but at the same time undergoes slight hydrolysis. It is at once hydrolysed by cold, moist silver oxide; slowly by heating with hydrochloric acid, with formation of picolinic acid hydrochloride. It is also very slowly hydrolysed by boiling water. Mixed with concentrated hydrochloric acid and kept in a vacuum over lime,

ethylic picolinate hydrochloride is formed in deliquescent crystals, yielding an orange crystalline *platinochloride* melting with decompotion at 154° (uncorr.). When boiled with water, this platinochloride decomposes, picolinic acid platinochloride being formed. *Ethylic picolinate ethiodide* crystallises in lemon-yellow scales melting at 104—105° (uncorr.), and is exceedingly soluble in water and alcohol, more sparingly in benzene and chloroform, and insoluble in ethylic iodide and in ether. The crystals belong to the rhombic system

$$[a : b : c = 0.7805 : 0.7737 : 1].$$

When treated with silver oxide, the ethiodide yields *picolinic acid ethylbetaine*, $C_5H_4NEtO_2$, crystallising in colourless plates or needles of bitter taste, and very soluble in water and alcohol. It gives no coloration with ferrous sulphate, and its salts are soluble in water. The *platinochloride*, $C_7H_{10}NO_2Cl,PtCl_4$, forms yellow scales melting with decomposition at 176°. When heated continuously at 100°, the betaïne evolves carbonic anhydride, and forms ethylpyridylium hydroxide. When heated with alcoholic ammonia at 105—110°, ethylic picolinate yields *picolinamide*, which crystallises in colourless, monoclinic needles, $a : b : c = 1.5588 : 1.3423 : 1$. It melts at 103.5°, sublimes, distils undecomposed, and is volatile in steam. It is sparingly soluble in light petroleum, easily so in the other usual solvents. When treated with bromine and dilute potash, it yields α-amidopyridine (Markwald, Abstr., 1893, i, 737); this melts at 92°, boils at 200° (uncorr.) (Markwald gives 56° and 204° respectively), and crystallises in glistening scales. The *hydrochloride* forms colourless, prismatic tables deliquescent in air; the *platinochloride* small triclinic needles $[a : b : c = 1.1735 : 0.6572 : 1]$, and melts at 227—228° (uncorr.). The yield of α-amidopyridine is, by this method, about 85 per cent. of the theoretical.

Ethylpyridylium hydroxide is also formed by acting on pyridine with potassium ethylic sulphate so that its formation as above may be from the previous formation of either the betaïne or of pyridine. The *mercurichloride*, $C_7H_{10}NCl,HgCl_2$, crystallises in white needles melting at 111.5°, and volatilises without leaving a residue; the *aurochloride*, $C_7H_{10}NCl,AuCl_3$, forms yellow needles melting at 141°; the platinochloride glistening rhombic plates

$$[a : b : c = 0.7080 : 0.7155 : 1],$$

melting at 193°. The author has prepared ethylpyridylium hydroxide by Anderson's method (*Annalen*, **94**, 358), and compared it with that prepared as above.

When treated with sodium in alcoholic solution by Ladenburg's method, ethylic picolinate yields ethylic pipecolinate; this forms deliquescent crystals, and gives a *platinochloride* melting at 110—112°.

Methylic picolinate is prepared in a similar way to the ethylic salt, but the heating must not be carried above 110—120°. It is a slightly yellow oil, of pleasant odour, boiling at 225—227° (uncorr.). Its *amide* melts at 103—104°. Methylpyridylium hydroxide is also formed, but only in small quantity.

The alkyl salts of picolinic acid are also formed by distilling a

mixture of potassium alkyl sulphate and potassium picolinate, but the yield is small. **L. T. T.**

Synthesis of Quinoline Derivatives. By S. NIEMENTOWSKI (*Ber.*, **27**, 1394—1403).—When anthranilic acid is heated for two or three days with acetophenone at 120—130°, 2'-phenyl-4'-hydroxyquinoline is formed. From metahomoanthranilic acid and acetophenone, 2-*methyl-2'-phenyl-4'-hydroxyquinoline* is formed; it crystallises in long plates, melts at 270°, and has both acid and basic properties. When boiled with ethylic acetoacetate, anthranilic acid yields two condensation products, namely, 2'-methyl-4'-hydroxyquinoline-3'-carboxylic acid, and, in larger quantity, a substance, $C_{22}H_{16}N_2O_5$, which appears to be an anhydride derived from 2 mols. of the first substance. This anhydride melts at 335°, and yields a *disodium salt*, (9H$_2$O); it is very stable to ordinary reagents, but, when distilled with zinc-dust, yields a mixture of quinoline and methylquinoline. Metahomoanthranilic acid yields with ethylic acetoacetate, in similar fashion, 2 : 2'-*dimethyl-4'-hydroxyquinoline-3'-carboxylic acid*, melting at 249°, and a substance, $C_{24}H_{20}N_2O_5$, melting above 350°. Ethylic ethylacetoacetate only forms the dimolecular compounds; with anthranilic acid, it yields a substance, $C_{26}H_{24}N_2O_5$, melting at 286°; with metahomoanthranilic acid, a substance, $C_{28}H_{28}N_2O_5$, melting above 345°. It will be noticed that all these substances which condense with anthranilic acid or its homologue contain the group —$CH_2 \cdot CO$—. In no case is the yield very satisfactory.

C. F. B.

Hexahydroquinoline. By H. TIETZE (*Ber.*, **27**, 1478—1481).— This substance, C_9NH_{13} (compare Bamberger and Lengfeld, Abstr., 1890, 1318), resembles the tetrahydro- more than the decahydro-compound. It boils at 224·5—225° under 712 mm. pressure; its *sulphate* melts at 174°; its *hydrochloride* at 171°. With phenylthiocarbimide, it yields *hexahydroquinolylphenylthiocarbamide*, $C_9NH_{12} \cdot CS \cdot NHPh$, melting at 127·5°; with phenylic cyanate, *hexahydroquinolylphenylcarbamide*, $C_9NH_{12} \cdot CO \cdot NHPh$, melting at 159—161°; with carbon bisulphide, *dihexahydroquinolylthiocarbamide*, $CS(C_9NH_{12})_2$, melting at 129°; with potash and benzoic chloride, *benzoylhexahydroquinoline*, $C_9NH_{12}Bz$, melting at 119—121°. When oxidised with alkaline permanganate, it yields benzoylanthranilic acid, together with benzamide, and benzoic and oxalic acids. Hexahydroquinoline absorbs 2 atoms of bromine, but the product is readily decomposed by water; if the resulting oil is shaken out with ether, and the ethereal solution treated with hydrogen bromide, white crystals of *monobromohexahydroquinoline hydrobromide*, melting at 184°, are obtained.

C. F. B.

Decahydroquinoline. By E. BAMBERGER and S. WILLIAMSON (*Ber.*, **27**, 1458—1478; compare Abstr., 1890, 1318).—Tetrahydroquinoline was reduced, as before, by heating with phosphorus and hydriodic acid. The product of the reaction is distilled with steam, when propylhexamethylene and propylbenzene distil over, together with an iodoquinoline derivative (probably diiododecahydroquinoline) that yields hexahydroquinoline when boiled with alcoholic potash.

Soda is added to the residue, and the distillation continued; deca-hydroquinoline now distils over, accompanied by hexahydroquinoline, which may be removed by shaking out the ethereal solution of the mixed bases with very dilute acetic acid.

Decahydroquinoline *picrate*, $C_9NH_{17},C_6H_3N_3O_7$, softens at 146°, and melts at 151—152°. The *chlorimide*, $C_9H_{16}NCl$, obtained by treating the base with bleaching powder solution, melts at 125·5°. The base itself, when treated with methylic iodide in ethereal solution, yields *dimethyldecahydroquinolinium iodide;* the *platinochloride*,

$$2C_9NH_{16}Me_2Cl,PtCl_4,$$

forms orange-red prisms melting with decomposition at 247°. When boiled for a long time with aqueous potassium methylic sulphate, it yields *methyldecahydroquinoline*, $C_9NH_{16}Me$, as a colourless, mobile oil, which boils at 204·5—205·5°, under 721 mm. pressure; it is alkaline to litmus, and absorbs carbonic anhydride; the yellow *aurochloride* melts at 109°; the *methiodide*, melting at 260°, is identical with the substance obtained by the direct action of methylic iodide on decahydroquinoline. Treated with aqueous potash and methylic chlorocarbonate, decahydroquinoline yields *methylic decahydro-quinolinecarbamate*, $C_9H_{16}N\cdot COOMe$; this is a colourless oil, boiling at 277—277·5° under 712 mm. pressure, and having an odour resembling that of peppermint. When added, in acetic acid solution, to a cooled acetic acid solution of fuming nitric acid, it yields a yellowish *mononitro-derivative* melting at 109°, and forming, with bromine, a *bromo*-derivative that melts at 170°. When it is treated with a larger quantity of undiluted fuming nitric acid at 10°, it is oxidised to *carboxymethylhexahydroorthoamidophenylacetic acid*,

$$COOMe\cdot NH\cdot C_6H_{10}\cdot CH_2\cdot COOH,$$

melting at 153·5°. When this is hydrolysed with hydrochloric acid, it yields a hydrochloride from which, by treatment with silver oxide, there is obtained a substance of high melting point that is possibly hexamethyleneoxindole, $C_6H_{10}{<}{\genfrac{}{}{0pt}{}{CH_2}{NH}}{>}CO$.

Benzoyldecahydroquinoline, prepared by treating the base with potash and benzoic chloride, melts at 96°, and boils at 352—354° under 714 mm. pressure. When oxidised with alkaline permanganate, it yields *maleinoid benzoylorthoamidohexahydrohydrocinnamic acid*, $NHBz\cdot C_6H_{10}\cdot CH_2\cdot CH_2\cdot COOH$, melting at 196°, together with small quantities of benzamide and benzoic acid, and an acid (? benzoyl-orthamidohexahydrocinnamic acid) melting at 153·5°, obtained in one experiment only, from which, after hydrolysis with hydrochloric acid, a substance was obtained that melts at 127°, and forms a hydro-chloride. When the above-mentioned maleinoïd benzoyl-acid is hydrolysed with hydrochloric acid at 160°, it yields *hexahydro-hydrocarbostyril*, $C_6H_{10}{<}{\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{NH\cdot CO}}$; this forms monoclinic crystals ($a:b:c = 1\cdot3178:1:0\cdot9953$; $\beta = 73°\ 34'$), melts at 151°, and sub-limes above 100°; its physiological action resembles that of oxy-piperidine. Its *benzoyl derivative*, melting at 85°, is obtained by

warming the maleinoïd benzoyl-acid for four hours with acetic chloride on the water bath; when hydrolysed with soda, it yields the maleinoïd benzoyl-acid; with hydrochloric acid, first this acid, and finally benzoic acid and hexahydrohydrocarbostyril. This last substance, when dissolved in aqueous soda and treated with benzoic chloride at 0°, yields *fumaroïd benzoylorthoamidohexahydrohydrocinnamic acid*, which melts at 205°, but with all reagents yields the same products as the maleinoïd isomeride described above; the isomerism is of the same kind as that of the hexahydrophthalic acids.

It will be seen that, generally speaking, decahydroquinoline and hexahydrohydrocarbostyril are respectively analogous, in their properties and reactions, to piperidine and oxypiperidine, to which they stand in the same relation as quinoline to pyridine.   C. F. B.

Phenylisoxazolonimide. By E. v. MEYER (*J. pr. Chem.*, [2], **49,** 504).—v. Rothenburg (this vol., i, 384) has overlooked the paper of Burns (Abstr., 1893, i, 314) which contains an account of the reaction between hydroxylamine and cyanacetophenone.

A. G. B.

n-Phenylpyrazolene. By R. v. ROTHENBURG (*Ber.*, **27,** 1265— 1266).—The author points out that one of the alternative constitutions assigned to the phenylpyrazolone (m. p. 118°) by Ruhemann and Morrell (this vol., i, 384) is identical with that which he assigned to the substance.   E. C. R.

Derivatives of Opiazone. By V. JACOBSON (*Ber.*, **27,** 1418— 1426).—When opiazone is heated with an alkali and methylic iodide (Abstr., 1893, i, 371), and the product evaporated with hydrochloric acid n-*methylnormethylopiazone*, $C_9H_7N_2O_3Me$, is obtained. This substance may also be prepared by heating opiazone with methylic iodide and methylic alcohol at 120°, and when pure melts at 144° (previously stated as 138°). The methylic group of one of the methoxyl-groups of the opiazone has, therefore, in this reaction wandered to the imido-group. A similar change occurs when opiazone is treated with benzylic chloride, n-*benzylnormethylopiazone*, $C_9H_7N_2O_3 \cdot C_7H_7$, being formed. This substance melts at 199—200°, and, like the methylic derivative, gives a blue coloration with ferric chloride. When amylic bromide is employed instead of the benzylic chloride, *normethylopiazone*, $C_9H_8N_2O_3$, is the sole product. This substance can be obtained from opiazone by the action of acids and by various other reactions. It crystallises in long, colourless needles, melts at 226°, and readily dissolves in water. It forms a yellow solution in alkalis, and gives a blue coloration with ferric chloride.

Acetylnormethylopiazone, $C_9H_7N_2O_3Ac$, is formed, along with the *diacetyl* compound, by the action of acetic anhydride on normethylopiazone. When the crude product is heated to about 200°, the diacetyl compound is decomposed with formation of acetic anhydride, and the pure monacetyl compound can then be obtained by recrystallisation. It forms prisms which melt at 209—210°, and gives no reaction with ferric chloride.

Noropiazone, $C_8H_6N_2O_3$, is obtained by heating opiazone with hydriodic acid; it forms small, colourless needles, melts at 302—305°, and is very sparingly soluble in water. *Triacetylnoropiazone*, $C_8H_3N_2O_3Ac_3$, melts at 184—186°, and when heated with water is partially decomposed. n-*Methylnoropiazone*, $C_8H_5N_2O_3Me$, is formed by molecular change when normethylopiazone is heated with hydriodic acid at 150°. It has a yellowish colour, and melts at 310°; with ferric chloride it gives a blue coloration.

Nitro-opiazone, $\begin{matrix} OMe\cdot C\cdot C(OMe)\cdot C\cdot CO\cdot NH \\ | \quad\quad\quad || \quad\quad | \\ CH\cdot C(NO_2)\cdot C\cdot CH\vcentcolon N \end{matrix}$, is prepared by the direct nitration of opiazone. It crystallises in matted, yellow needles, melting and decomposing at 248°. The same compound may be obtained by the action of hydrazine on nitro-opianic acid. Nitro-opiazone possesses acid properties, and forms a red, soluble *potassium* salt, $C_{10}H_8N_3O_5K$, the imido-hydrogen being replaced. n-*Methylnitronormethylopiazone*, $NO_2\cdot C_9H_6N_2O_3Me$, is formed when nitro-opiazone is heated with methylic iodide and methylic alcohol at 150°. It crystallises in red needles, decomposes at 286°, and gives a greenish-brown coloration with ferric chloride. Like nitro-opiazone, it is an acid, and forms a *potassium* salt.

This red *n*-methylnitronormethylopiazone is accompanied by a yellow isomeric compound, which crystallises in prisms and 'melts at 186°. The isomerism is probably due to the participation of both of the methoxyl groups in the molecular change.

Chloropiazone cannot be converted into chloronormethylopiazone, since the chlorine atom enters into the reaction, and normethylopiazone is formed. A. H.

Morphine. By L. KNORR (*Ber.,* **27,** 1144—1150; compare Abstr., 1889, 417, 905).—It has been previously shown that methylmorphimethine, on treatment with acetic anhydride, is resolved into methoxyhydroxyphenanthrene and hydroxyethyldiethylamine, the amorphous base, which is also formed, proves to be optically isomeric with methylmorphimethine, and is termed the β-form. It differs from α-methylmorphimethine (m. p. 118·5°) as follows: It is more readily soluble in ether, the specific refractive power $[\alpha/D]^{17} = +437\cdot3$ $(c = 3\cdot746)$, with sulphuric acid it gives a violet coloration, changing successively to blue and green on dilution; the lethal dose is twice as great. The *hydrochloride* and *tartarate* are readily soluble; the methiodide crystallises in needles, melts at 297°, and was previously obtained by Hesse, who, however, overlooked its optical relationship to the α-derivative; the specific rotatory power $[\alpha/D]^{17} = +227\cdot45$ $(c = 1\cdot248)$. The acetyl derivative and its *methiodide* are not crystalline. Methylmorphimethine is completely decomposed by hydrochloric acid, but, by the action of hydrogen chloride at 180°, it is resolved into dihydroxyphenanthrene, methylic chloride, water, and probably chlorethyldiethylamine; part of the base is recovered as β-methylmorphimethine. The dihydroxyphenanthrene was identified by its acetyl-derivative (m. p. 158°), and has been previously prepared by v. Gerichten and O. Fischer. On distillation with zinc dust, methylmorphimethine yields 10 per cent. of its weight of phen-

anthrene, whilst from morphine only 3—4 per cent. is formed. These results are in complete accord with the formula

$$OMe \cdot C_{10}H_5 {<}^{CH(OH)}_{CH\,:\,CH}{>}CH \cdot O \cdot C_2H_4 \cdot NMe_2,$$
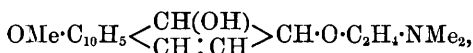
for methylmorphimethine previously suggested by the author.

Methylmorphimethine is readily prepared by the following method : Sodium (24 grams) is dissolved in methylic alcohol (1 litre), commercial morphine (303 grams), and methylic iodide (350 grams) added, the yield of codeïne methiodide is 90 per cent. of the theoretical. The iodide (400 grams) is dissolved in water (2 litres) and boiled for 10 minutes with 25 per cent. soda (500 c.c.). The yield of pure base is 80 per cent. of the theoretical. Codeïne methiodide decomposes at 270° ; its specific refractive power $[\alpha/D]^{17} = -81\cdot9°$. α- and β-methylmorphimethine differ considerably from morphine and codeïne in their physiological action ; they lower the blood pressure, reduce the heart's activity, and possess no anæsthetic or soporific action, neither do they cause contraction of the pupil.

<div style="text-align:right">J. B. T.</div>

Codeïne. By W. GÖHLICH (*Arch. Pharm.*, **232**, 154—160 ; compare Abstr., 1893, i, 675).—Dicodeïne ethylene bromide,

$$(C_{18}H_{21}NO_3)_2,C_2H_4Br_2 + 4H_2O,$$

has been obtained in crystals which soften at 155—157°, and melt at 177—179°. It remains colourless with cold sulphuric acid, becoming blue when heated; a yellow coloration is produced by nitric acid. Erdmann's reagent gives a yellow colour, changing to blue on heating ; with vanadic anhydride and sulphuric acid a yellow coloration is developed which turns green, and finally blue on heating ; the same effect is produced by Fröhde's reagent. Dicodeïne ethylene bromide gives Faby's reaction for codeïne, and when warmed with concentrated sulphuric acid and a small quantity of cane sugar, produces a brilliant purple coloration. Its aqueous solution is lævorotatory, and gives $[\alpha]_D = -97\cdot06°$ at 20°. Dicodeïne ethylene bromide belongs to the rhombic system, $a : b : c = 0\cdot9601 : 1 : 0\cdot8292$.

Dicodeïne ethylene chloride, $(C_{18}H_{21}NO_3)_2,C_2H_4Cl_2 + 4H_2O$, is obtained by treating the above-mentioned substance with silver chloride. It forms colourless needles which soften at 164—168°, and melt at 182—192° ; the colour reactions correspond exactly with those of the previous compound.

<div style="text-align:right">M. O. F.</div>

Constitution of Cinchonine. By W. v. MILLER and G. ROHDE (*Ber.*, **27**, 1187—1190).—When methylcinchonine and phenylhydrazine are heated together in acetic solution a crystalline *hydrazone*, $C_{26}H_{30}N_4$, is formed which melts at 151·5°. It is basic in properties, and dissolves in acids. Ethylcinchonine, methylquinine, and methylquinidine behave similarly. The *hydrazone*, $C_{27}H_{32}N_4$, from ethylcinchonine melts at 152—153°. The *hydrazones* from methylquinidine and methylquinine both melt at 135—136°, have the same crystalline form, and appear to be identical. These results show that in methylcinchonine the oxygen is in the aldehydic or ketonic form.

The authors then discuss the bearing of these facts and the results recently obtained by Skraup, Koenigs, and others on the question of the constitution of one part of the cinchonine molecule.　　L. T. T.

Constitution of Cinchonine. By W. v. MILLER and G. ROHDE (*Ber.*, **27**, 1279—1281; compare preceding Abstr.).—Cinchonine, when heated with dilute acetic acid for 24 hours at 105°, yields an oil having the appearance of methylquinine and methylquinidine. It gives a purple coloration with diazobenzene sulphonic acid and a few drops of alkali; when warmed with moist silver oxide in alcoholic solution, it reduces it with the formation of a mirror, and yields a hydrazone with phenylhydrazine. When treated with methylic iodide and soda, it yields methylcinchonine (m. p. 74—75°) and its methiodide. The above reactions are in accordance with the authors' views on the constitution of cinchonine.　　E. C. R.

Non-existence of Chenopodine. By G. BAUMERT and K. HALPERN (*Arch. Pharm.*, **231**, 648—653).—See this vol., ii, 370.

Cholic acid. By K. LANDSTEINER (*Zeit. physiol. Chem.*, **19**, 285—288).—Bromine acts destructively on dry cholic acid; it is slowly absorbed by a solution in acetic acid with evolution of hydrogen bromide.

Bromdehydrocholic acid, $C_{24}H_{33}BrO_5$, is obtained by the bromination of dehydrocholic acid in acetic acid solution; it crystallises in needles, and melts and decomposes at 171—173°. Small, octahedral crystals melting at 160—163° were also obtained, and seemed to be a mixture of the foregoing substance with an isomeride or other substance. The bromination can be carried further, but the crystalline product obtained does not seem to have been examined.

Bilianic acid also seems to yield a substitution derivative with bromine.

When treated with fuming nitric acid at 0°, cholic acid is converted into dehydrocholic acid.　　　A. J. G.

Action of Zinc and its Salts on Blood and Blood-pigment. By E. GRAHE (*Chem. Centr.*, 1894, i, 636—637; from *Arb. Pharmak. Inst. Dorpat*, **9**, 155—174).—By shaking blood with zinc dust Kobert has prepared zinc-parahæmoglobin. This substance resembles oxyhæmoglobin in spectrum and in solubility in dilute ammonia; it resembles methæmoglobin in colour and other properties. It differs from both in certain solubilities and colour reactions. It can be prepared by the use of many zinc salts, both from blood and solutions of crystalline blood-pigment. It is precipitated by hydrochloric acid from alkaline solutions, and the formula $C_{758}H_{1139}Zn_2S_3FeO_{218}$ is given to it. It is not toxic, and like hæmoglobin is absorbed, and of use in the treatment of chlorosis.　　　W. D. H.

Organic Chemistry.

Possible Number of Isomerides of a Carbon Compound. By DELANNOY (*Bull. Soc. Chim.*, [3], **11**, 239—248).—The author has investigated the general problem respecting the possible number of isomerides of a carbon compound by a process somewhat similar to that used by Cayley; his results, however, differ slightly from those of the latter. W. J. P.

Aspen Tar. By W. ADOLPHI (*Arch. Pharm.*, **232**, 321—328).— Aspen tar from *Populus tremula* is a commercial article in Central Russia. It is a black, oily liquid of sp. gr. 1·0586 at 15°, and has a peculiar and unpleasant odour; the crystalline leaflets which are visible in the body of the liquid do not give the reactions of pimaric acid. The tar is completely soluble in absolute alcohol, acetone, or alkalis, and 72 per cent. of it distils below 300°, leaving a little pitchy residue. The distillate contains acetic, propionic, butyric, valeric, and caproic acids. The phenols present form 16·7 per cent. of the tar distilled, and boil at 200—290°, more than half distilling at 250—270°; the fraction boiling at 230° gives the catechol reaction, whilst the portions boiling at higher temperatures give the pyrogallol reaction with ferric chloride; guaiacol is also present. The hydrocarbons boil at 100—340°, the major part distilling at 210—260°; paraffin melting at 38° was isolated from the fraction boiling at 290—340°. W. J. P.

Trimethylene and Propylene, and a New Class of Hydrocarbons: Dynamic Isomerism. By BERTHELOT (*Compt. rend.*, **118**, 1115—1123).—The author has previously shown that the heat of formation of propylene from its elements is —9·4 Cal., and of trimethylene —17·1 Cal. From Louguinine's determinations of the heats of combustion, it follows that the heats of formation of the two alcohols from their elements are +80·6 Cal. and +78·6 Cal. respectively.

Direct determination of the heat developed by the combination of bromine with propylene shows that

$$C_3H_6 + Br_2 \text{ liquid} = C_3H_6Br_2 \text{ liquid develops} + 29\cdot1 \text{ Cal.}$$
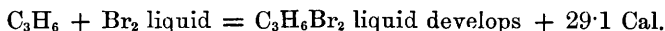
This value is almost identical with the corresponding value in the case of ethylene +29·3 Cals., and it follows that propylene is the true homologue of ethylene. There is, moreover, the normal difference between the heats of formation of the two hydrocarbons.

In the case of trimethylene, the number obtained is much higher.

$$C_3H_6 \text{ (trimethylene)} + Br_2 \text{ liq.} = C_3H_6Br_2 \text{ liq. develops} + 38\cdot5 \text{ Cal.}$$
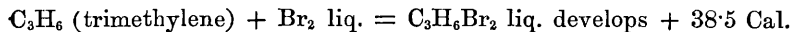
Both dibromides develop a further quantity of heat in contact with an excess of bromine, owing to the formation of perbromides, and the

values obtained are somewhat higher in the case of trimethylene, but the difference is not great.

In the calorimeter, the absorption of propylene by sulphuric acid takes place less readily than in an eprouvette, and it is not possible to obtain complete saturation of the acid. The results with very different proportions of acid do not, however, differ materially.

$$C_3H_6 + H_2SO_4 \text{ liquid develops } +16\cdot5 \text{ Cal.}$$
$$2C_3H_6 + 3H_2SO_4 \quad ,, \qquad ., \quad +16\cdot7 \times 2 \text{ Cal.}$$
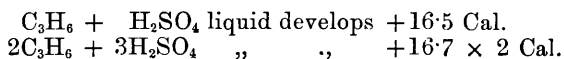
Some years ago, with a large excess of sulphuric acid, the author obtained the value $+19\cdot0$ Cal. If the results are calculated for a dilute acid (which does not actually absorb the gas), it is found that

$$C_3H_6 + H_2SO_4 \text{ dilute, develops } +16\cdot7 \text{ Cal.}$$
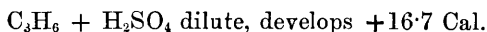
a number practically identical with that obtained with ethylene, $+16\cdot9$ Cal.

When sulphuric acid completely saturated with propylene is brought in contact with water, there is practically no development of heat (this vol., i, 393), but if a considerable quantity of free sulphuric acid is present, precautions must be taken to avoid any appreciable rise of temperature, or the propylene sulphate is decomposed and isomerides of propylene are formed. Trimethylene sulphate, although more stable in presence of water, likewise decomposes if any rise of temperature is allowed to take place when the partially saturated sulphuric acid is mixed with water.

In the case of trimethylene sulphate, the values obtained are

$$2C_3H_6 + 3H_2SO_4 \text{ liquid develops } +25\cdot5 \times 2 \text{ Cal.}$$
$$C_3H_6 + 3H_2SO_4 \quad ,, \qquad ,, \quad +26\cdot2 \text{ Cal.}$$
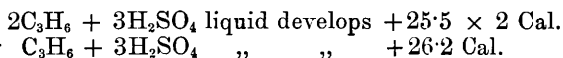
Hence, for the same proportions of gas absorbed, the values are for propylene $+16\cdot7$ Cal., and trimethylene $+25\cdot5$ Cal.

It will be observed that the heats of formation of the trimethylene compounds are from 8 to 10 Cals. in excess of the heats of formation of the corresponding propylene compounds, whereas in the case of the hydrocarbons themselves the difference has a similar numerical value but is opposite in sign. The heats of formation of the two series of compounds from their elements are, however, practically the same for the corresponding members. Similar differences have been observed by the author and Matignon between terebenthene and its isomerides. The former has the lower heat of formation from its elements, but the heat of formation of its hydrochloride by the action of hydrogen chloride is double that of its isomerides, whilst the heats of formation of the hydrochlorides from their elements are almost identical.

Trimethylene and terebenthene, respectively, differ from their isomerides in a manner that cannot be represented by plane formulæ. They represent new types, characterised by their mobility and their reserves of energy. The author terms them *dynamic isomerides*. The explosive liquid polymerides of acetylene perhaps belong to the same class.   C. H. B.

Rectification of Alcohol. By E. SOREL (*Compt. rend.*, **118**, 1213—1215).—The author has previously shown that in the rectification of alcohol the volatile impurities ascend to higher levels, or descend towards the still, according as the difference $K - P/p$ is positive or negative, K being the ratio of the weight of the impurity in 1 kilo. of the vapour and in 1 kilo. of the liquid in contact with the particular level, P the weight of the liquid that flows back, and p the weight of the vapour that passes upwards at that level. He has now determined the values of K for fermentation isoamylic alcohol, ethylic formate, methylic acetate, ethylic acetate, ethylic isobutyrate, ethylic isovalerate, isoamylic acetate, and isoamylic isovalerate, and the results are given in a table. The value of K increases with increase of molecular weight and rise of boiling point, but there is no definite relation between the three. In each group, however, the value of K increases the more dilute the alcohol. Ethylic formate and methylic acetate are soluble in water or dilute alcohol, and in these cases the ratio of the values of K for a given alcoholic strength increases continuously with the proportion of water. Ethylic isovalerate and isoamylic acetate are insoluble in dilute alcohol, and the ratio passes through a maximum. Ethylic isobutyrate and the ethereal salts of higher molecular weight can only be retained in the rectifying column in presence of strong alcohol. C. H. B.

Constitution of Licareol. By P. BARBIER and L. BOUVEAULT (*Compt. rend.*, **118**, 1208—1211).—When licareol is gradually mixed with sufficient chromic acid mixture to yield 2 atoms of oxygen for each molecule of the alcohol, it yields acetone, licaraldehyde or lica-rhodal, a methyl heptylene ketone, acetic and formic acids, and methylheptyleneketonecarboxylic acid. With an excess of boiling chromic acid mixture, the products are formic and acetic acids and terebic acid.

The licaraldehyde boils at 111—112° under a pressure of about 13 mm., and yields an oxime boiling at about 145° under a pressure of 12 mm., which in its turn yields licarionitrile, boiling at 110—111° under a pressure of 13 mm. It yields with paramidophenol a crystalline compound, $C_{10}H_{16}N \cdot C_6H_4 \cdot OH$. When boiled with glacial acetic acid, it yields paracymene.

The methyl heptylene ketone is identical in all its properties with the natural product.

The formation of terebic acid indicates that the constitution of licareol is more probably $CMe_2 {:} CH \cdot CH_2 \cdot CH(CH_2 \cdot OH) \cdot CMe {:} CH_2$ than that previously ascribed to it. Licareol and lemonol (geraniol) yield practically the same products on oxidation, and the only reasons for supposing that they have different constitutions are that the former is optically active whilst the latter is inactive, and the two aldehydes yield, with paramidophenol, compounds which have different melting points. It is possible, although not probable, that lemonol is a racemic compound. C. H. B.

Geraniol from Oil of "Andropogon Schœnanthus." By P. BARBIER and L. BOUVEAULT (*Compt. rend.*, **118**, 1154—1157).—When

geraniol from oil of *Andropogon Schœnanthus* is allowed to fall drop by drop into a boiling chromic acid mixture capable of yielding 10 atoms of oxygen for each molecule of alcohol, the products are carbonic anhydride, acetone, acetic and formic acids, and terebic acid (m. p. 174°). No valeric acid is formed.

When a quantity of chromic acid mixture, capable of yielding 2 atoms of oxygen for each molecule of the alcohol, is added little by little to the geraniol, the products are geranaldehyde, boiling at 113° under a pressure of 13 mm., and identical with so-called citriodoric aldehyde; methyl heptylene ketone, boiling at 169—172°, possessing all the properties of the natural product, and not yielding the crystalline bromine derivative described by Tiemann and Semmler; paracymene, formed as a secondary product by the action of the sulphuric acid on the geranaldehyde; and methylheptyleneketone-carboxylic acid. .

With potassium permanganate, the geraniol yields no valeric acid. It follows that the geraniol of *Andropogon Schœnanthus* has the constitution $CH_2:CMe\cdot CH_2\cdot CH_2\cdot CMe_2\cdot CH_2\cdot OH$.

Oil of pelargonium is quite different from oil of *A. Schœnanthus*, and hence it is undesirable to retain the name of geraniol for the oil contained in the latter. The author proposes to call it *lemonol*.

C. H. B.

Inverting Action of Glycerol. By E. DONATH (*J. pr. Chem.*, [2], **49**, 546—548).—Consideration of Zulkowski's work on the transformation of starch in hot glycerol (Abstr., 1889, 116) led the author to ascertain whether glycerol has any hydrolytic action on sugars. It was found that cane sugar, milk sugar, maltose, and raffinose are hydrolysed when heated at 120—130° with aqueous glycerol in the same manner as they are hydrolysed by dilute acids; furthermore, the order of facility with which the hydrolysis occurs is the same, whether glycerol or acid be the hydrolytic agent. Anhydrous glycerol has comparatively little hydrolytic action, whilst glycerol containing 20 per cent. of water has a considerable action; from this the author concludes that the hydrates of glycerol contained in the aqueous solution are dissociated at the temperature employed, and that it is the nascent molecules of water of hydration which effect the hydrolysis. It is hoped that a general theory of hydrolytic action may be deduced from these observations.

A. G. B.

Ethylnitrolic acid and Nitromethane. By V. MEYER (*Ber.*, **27**, 1600—1602).—*Benzoylethylnitrolic acid*, $NO_2\cdot CMe:N\cdot OBz$, may be readily prepared by agitating ethylnitrolic acid with caustic soda and benzoic chloride. It crystallises from toluene in small, white plates, and melts at 137° without decomposing. When boiled with dilute sulphuric acid, it decomposes into nitrous oxide, and acetic and benzoic acids. The compound may be preserved without undergoing any change, whilst the nitrolic acids themselves soon decompose.

Sodionitromethane has hitherto never been obtained pure, the composition of the salt prepared by means of alcoholic soda always

agreeing with the formula $CH_2Na\cdot NO_2 + 2\frac{1}{2}H_2O$. When, however, a solution of sodium ethoxide is added to a solution of nitromethane in ether, the pure substance is at once precipitated. The compound thus prepared is much more violently explosive than that previously obtained. A. H.

Action of Thiocarbonic Chloride on Ethylenediamine. By M. JAFFÉ and B. KÜHN (*Ber.*, **27**, 1663—1666).—The action takes place according to the equation $2CSCl_2 + 2C_2H_4(NH_2)_2 = C_6H_{10}N_4S + 4HCl + H_2S$. The substance $C_6H_{10}N_4S$ appears to have the con-

$$\begin{array}{c} CH_2\cdot N:C\cdot NH\cdot CH_2 \\ \mid \qquad S \qquad \mid \\ CH_2\cdot NH\cdot C:N\cdot CH_2 \end{array}$$

stitution, and probably results from the elimina-

tion of H_2S from the tautomeric form of the compound

$$\begin{array}{c} CH_2\cdot NH\cdot CS\cdot NH\cdot CH_2 \\ CH_2\cdot NH\cdot CS\cdot NH\cdot CH_2 \end{array},$$
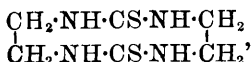
which may be supposed to be first formed. It readily loses its sulphur under the influence of mild oxidising agents, such as bromine water, yielding a substance, the hydrobromide of which, $C_6H_{10}N_4,HBr$, was obtained crystallised. It forms various salts, of which the formulæ and melting points (with decomposition) are :—$C_6H_{10}N_4S,HCl$; 270°. $C_6H_{10}N_4S,HNO_3$; 246—247°. $C_6H_{10}N_4S,H_2SO_4$; 230—231°. $C_6H_{10}N_4S,HgCl_2$. $C_6H_{10}N_4S,HCl,2HgCl_2$. $C_6H_{10}N_4S,C_6H_3N_3O_7$ (picrate); 229—230°. C. F. B.

Choline and Muscarine. By G. NOTHNAGEL (*Arch. Pharm.*, **232**, 261—306; compare Abstr., 1892, 219, 806; 1893, i, 297).— *Acetylethyltrimethylammonium platinochloride*, $(OAc\cdot C_2H_4\cdot NMe_3)_2PtCl_6$, crystallises in small, yellow needles melting at 223—224°. Choline only reacts with acetic chloride at 100°, and the acetyl compound is readily hydrolysed.

On heating choline chloride with benzoic chloride at 100°, distilling off the excess of the latter, and treating the residue with platinic chloride in aqueous solution, yellow, crystalline threads of a *platino-chloride*, $(OBz\cdot C_2H_4\cdot NMe_3)_2PtCl_6$, are deposited; it melts at 206°. The *aurochloride*, $OBz\cdot C_2H_4\cdot NMe_3\cdot AuCl_4$, crystallises in flat, yellow needles melting at 183°. No reaction between choline and glycollic, salicylic, or ethylenelactic acid could be brought about under various conditions.

On heating an aqueous solution of choline with hydroxyisobutyric acid, a substance is formed, which yields a *platinochloride* of the constitution $NMe_3Cl\cdot C_2H_4\cdot O\cdot CMe_2\cdot COO\cdot C_2H_4\cdot NMe_3Cl,PtCl_4 + 2H_2O$; it crystallises in needles melting at 221°. No aurochloride could be prepared either directly or from the platinochloride, the latter, when treated with gold chloride, decomposing with formation of choline aurochloride. Similarly, on heating choline solution with hydroxyvaleric acid and treating the product with platinic chloride, a *platinochloride* of the composition $NMe_3Cl\cdot C_2H_4\cdot O\cdot C_4H_6\cdot COO\cdot C_2H_4\cdot NMe_3Cl,PtCl_4 + 2H_2O$,

is obtained; it crystallises in long, compact needles melting at 223—224°. No aurochloride could be prepared.

The rest of the paper consists principally of a repetition and confirmation of previous work on this subject.   W. J. P.

Diazomethane. By H. v. PECHMANN (*Ber.*, **27**, 1888—1891).— When nitrosomethylbenzamide, nitrosomethylurethane, and similar nitroso-derivatives of methylamine are treated with alkalis, a yellow gas is formed, along with other products. This gas is *diazomethane*, $CH_2<\frac{N}{N}$. It is odourless, but very poisonous, and has hitherto only been examined in ethereal solution. The yellow, ethereal solution is at once decolorised by dilute acids or by water, the whole of the nitrogen being evolved. Iodine solution also decomposes it, nitrogen being evolved and methylene iodide formed. Like ethylic diazo-acetate, it combines with ethylic fumarate, and forms *methylic pyrazoline*-4 : 5-*dicarboxylate*, which crystallises in lustrous, rhombic tablets melting at 97°. When this substance is heated with dilute hydrochloric acid, hydrazine hydrochloride is produced. When the pyrazoline-derivative is distilled, decomposition occurs, about 80 per cent. of the nitrogen being evolved, and cistrans-trimethylene-1 : 2-dicarboxylic acid passing over.

Diazomethane behaves towards silver nitrate and Fehling's solution in the same manner as ethylic diazoacetate, reduces mercuric oxide in the cold, and rapidly bleaches and destroys cork.

Diazoethane has been prepared in a similar manner, and has similar properties: when it is treated with mercuric oxide, the smell of mercuric ethide is perceptible.

A more detailed account will be shortly published.   A. H.

Compounds of Formaldehyde with Polyhydric Alcohols. By M. SCHULZ and B. TOLLENS (*Ber.*, **27**, 1892—1894).—When the polyhydric alcohols are heated on the water-bath with a 40 per cent. solution of formaldehyde and concentrated hydrochloric acid, a reaction occurs, and methylene ethers or formacetals are produced.

Mannitoltriformacetal, $C_6H_8O_6(CH_2)_3$, forms needles melting at 227°, and sparingly soluble in water and alcohol. It is lævo-rotatory. *Sorbitoltriformacetal* melts at 206°, and otherwise resembles the mannitol compound. *Adonitoldiformacetal*, $C_5H_7O_4(CH_2)_2\cdot OH$, melts at 145°, may be sublimed in a vacuum, and is more readily soluble than the mannitol-derivative. One hydroxyl group is left in the compound, since it forms a *benzoate* which melts at 104°. *Penta-erythritoldiformacetal*, $C_5H_8O_4(CH_2)_2$, forms large crystals melting at 50°, very readily soluble in water. Erythritol yields a similar compound. *Glycerolformacetal*, $C_3H_5O_2(CH_2)_2OH$, is a liquid boiling at 191—193°, and forms a *benzoate* melting at 70°.   A. H.

Condensation of Methyl Ethyl Ketone with Malonic acid. By W. MASSOT (*Ber.*, **27**, 1574—1577).—When methyl ethyl ketone and malonic acid are heated together with acetic anhydride, the pro-

duct consists of two portions, one crystalline, the other oily. The crystalline product is a monobasic acid of the formula $C_9H_{10}O_4$, which crystallises from light petroleum in small prisms melting at 76—77°. The *barium* salt $(C_9H_9O_4)_2Ba + H_2O$, forms microcrystalline crusts. When treated with alkaline hydroxylamine solution, the acid yields a *monoxime*, $C_9H_{10}O_3$:N·OH, which forms small, prismatic crystals, and melts at 195—196°. A dioxime could not be obtained, neither could any evidence of the presence of a hydroxyl-group be found; the constitution of the acid, therefore, remains unsettled, but it appears to be the homologue of the acid, $C_8H_8O_4$, obtained by the author from acetone and malonic acid (this vol., i, 356), and, like this, is only formed in very small quantity.

The oily product contains a certain amount of the above acid, together with β-ethylcrotonic acid, CMeEt:CH·COOH, which, however, could not be obtained pure.   A. H.

Diamidopropionic acid. By E. KLEBS (*Zeit. physiol. Chem.*, **19**, 301—338; compare Abstr., 1893, i, 686).—The author gives a table showing the behaviour of diamidopropionic acid towards reagents. The *mercuric* salt, $(NH_2·CH_2·CH(NH_2)·COO)_2Hg,4H_2O$, is obtained in colourless cubic crystals; both this and the copper salt have an alkaline reaction, and give no precipitates with caustic soda even on boiling. The *sulphate* crystallises in needles containing $\frac{1}{2}H_2O$, and melts and decomposes at 226—228°. The *nitrate* crystallises without water, and melts and gives off gas at 170°. The *acetate* is obtained in small, anhydrous, orthorhombic plates melting at 110—112°; on prolonged heating at 100°, it melts and gives off acetic acid. The *oxalate* crystallises in small needles containing $2H_2O$, and melts and decomposes at 175—178°. The *picrate* decomposes at 200°, and resembles picric acid in appearance; it crystallises with $2H_2O$. The *platinochloride* crystallises in tiny cubes containing $1H_2O$.

Diamidopropionic acid yields glyceric and oxalic acids when treated with nitrous acid.

Dibenzoyldiamidopropionic acid, NHBz·CH₂·CH(NHBz)·COOH, is prepared by treating diamidopropionic acid hydrochloride with benzoic chloride and caustic soda; it crystallises in colourless needles melting at 195—197°, and is very sparingly soluble in water. The *barium* salt forms white, anhydrous crystalline crusts.

Attempts to synthesise diamidoacetic acid by the action of ammonia on dihalogenacetic acids or their ethylic salts, by the reduction of ethylic formazylcarboxylate and, indirectly, by the action of mercuracetamide on ethylic diiodoacetate were unsuccessful.

W. J. P.

Action of Water on Soap. By F. KRAFFT and A. STERN (*Ber.*, **27**, 1747—1754).—In view of the recent theories as to the cleansing action of soap (see next abstract), the authors have repeated and extended Chevreul's experiments on the action of water on soap, and have confirmed the results arrived at by him. When neutral sodium palmitate, $NaC_{16}H_{31}O_2$, containing 8·27 per cent. of sodium, is boiled up with water and the liquid allowed to cool, the mass which separates contains less sodium as the amount of water employed is

increased. When about 900 parts of water are used, the mass which separates has the composition of sodium bipalmitate,

$$C_{16}H_{32}O_2,C_{16}H_{31}O_2Na,$$

whilst, with smaller quantities of water, any desired mixture containing more sodium than this may be obtained. The filtrate from the solid mass has a strongly alkaline reaction, and is almost free from fatty acid, the addition of a mineral acid producing only a faint turbidity, so that basic salts are certainly not present. A hot dilute solution of sodium palmitate has a milky appearance, which is due to the presence of free palmitic acid in the form of oily drops suspended in the liquid. When such a solution is extracted with toluene, pure palmitic acid goes into solution. The hot solution therefore contains free fatty acid as well as free alkali, which may be titrated with normal acid, in addition to a certain amount of undecomposed sodium salt.

Sodium stearate and sodium elaïdate behave in a precisely similar manner, but sodium oleate is not so readily decomposed by hot water, only a very slight turbidity being caused by the addition of 900 parts of hot water. Sodium bioleate, on the other hand, is at once decomposed by water with separation of free oleïc acid.　　A. H.

The Cleansing Action of Soap. By F. KRAFFT and A. STERN (*Ber.*, **27**, 1755—1761; compare the foregoing abstract).—The authors criticise the view put forward by Rotondi [*Atti R. Accad. sci. Torino*, **19**, 146 (1883)] and others, that when soap is acted on by water it is decomposed into an acid soap, which is almost insoluble in hot water, and a basic soap which remains dissolved. It follows from the experiments described in the foregoing abstract that when a soap is dissolved in a large amount of hot water, the sodium salts of palmitic, stearic, and elaïdic acids separate out, along with an amount of the free acid which varies with the amount of water used, whilst the liquid contains free alkali and the sodium salt of oleic acid. No evidence of the existence of basic salts of the soap acids has been brought forward by the supporters of the theory, and none could be experimentally obtained by the authors.　　A. H.

Chemical Function and Constitution of Ethylic Aceto-acetate. By DE FORCRAND (*Compt. rend.*, **118**, 1101—1104).—The author has previously shown that the heat of dissolution of ethylic aceto-sodacetate is $+4\cdot39$ Cals. (this vol., i, 356), and he now finds that the heat of dissolution of ethylic acetoacetate is $+1\cdot25$ Cals., and its heat of neutralisation by sodium hydroxide $+7\cdot32$ Cals. It follows that

$C_6H_{10}O_3$ liq. $+$ Na sol. $=$ H gas $+$
　$C_6H_9NaO_3$ sol. .... develops $+47\cdot26$ Cals.
$C_6H_{10}O_3$ liq. $+$ NaOH sol. $=$ H$_2$O sol. $+$
　$C_6H_9NaO_3$ sol. ....　　,,　　$+16\cdot39$　,,
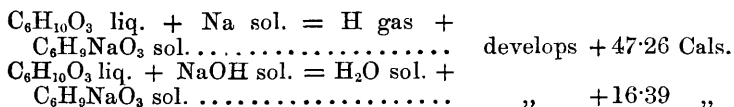
If the first of these values is taken as the measure of the acid function, it is clear that it is lower than that of a true acid, but higher

than that of a tertiary alcohol. For the latter reason, the constitution of the compound cannot be $CH_3 \cdot C(ONa) \colon CH \cdot COOEt$. The value of the acid function when calculated for the solid state of the original substance is not below 39 Cals. The only formula admissible would therefore seem to be $CH_3 \cdot CO \cdot CH_2 \cdot COOEt$ and $CH_3 \cdot CO \colon CHNa \cdot COOEt$, although, in its chemical behaviour, the compound differs in many respects from ketones.

Attempts to prepare a pure sodium derivative of acetone, and thus determine directly the value of the ketonic function, were unsuccessful. All that is definitely known in this connection is (1) that the thermal value of the ketonic function is lower than that of the primary alcoholic function, and (2) the heat of neutralisation of a ketone is *nil*. It would seem certain that ethylic acetoacetate has not a ketonic function. There is, however, close agreement between the value of the phenolic function ($+39 \cdot 1$ Cals.) and the heat of neutralisation of ordinary phenol ($+7 \cdot 96$ Cals.) and the corresponding values for ethylic acetoacetate ($+39$ to 40 Cals. and $+7 \cdot 32$ Cals. respectively). If it is assumed that the cause of the special acidity of the phenols is due not so much to the closing of the hydrocarbon chain as to the peculiar nature of the linkage of the carbon which is united with the hydroxyl group, it would seem that ethylic acetoacetate may be regarded as an open chain phenol with a degree of acidity intermediate between the true acids and alcohols. Its constitution would then be $CH_3 \cdot C(OH) \colon CH \cdot COOEt$. C. H. B.

$\alpha_1 \alpha_2$-**Dimethyladipic acids.** By J. KITZING (*Ber.*, **27**, 1578—1580).—When ethylene dibromide is heated with ethylic sodiomethylmalonate in the presence of toluene for 50—60 hours, *ethylic $\alpha_1 \alpha_2$-dimethyldicarboxyadipate*, $C_2H_4 \cdot [CMe \cdot (COOEt)_2]_2$, is obtained. It separates from light petroleum in well-developed crystals melting at 53—53·5°, and can be distilled under diminished pressure. $\alpha_1 \alpha_2$-*Dimethyldicarboxyadipic acid*, when rapidly heated, melts and decomposes at about 200°, but, when slowly heated, decomposes at about 170°, dimethyladipic acid (Zelinsky, Abstr., 1892, 430) being formed; both the modification melting at 140—141° and that melting at 74—76° are obtained by recrystallising the product from water. A. H.

Bromomesaconic acid. By W. LOSSEN and O. GERLACH (*Ber.*, **27**, 1851—1856).—As shown by Kekulé and others, citradibromoglutaric acid is resolved by the action of bases into bromomethacrylic acid, carbonic anhydride, and hydrogen bromide; under other conditions, propaldehyde, carbonic anhydride, and hydrogen bromide are formed. In continuation of their investigation of the influence exercised by the quantity and nature of the base on the decomposition of haloïd acids (Abstr., 1893, i, 142), the authors have found that by the action of concentrated (25 per cent.) soda (4 mol.) on citradibromoglutaric acid, *bromomesaconic acid*, $C_3H_3Br(COOH)_2$, is formed, and crystallises from ether, on the addition of chloroform, in colourless stellate prisms melting at 220°. The yield is about 47 per cent. of the bromoglutaric acid employed. By the further action of soda bromomesaconic acid is converted into acetic acid; on reduction,

it yields glutaric acid, and, by heating above its melting point, bromocitraconic anhydride is produced. The *hydrogen potassium salt*, $C_5H_4BrO_4K$, crystallises in prisms; the *barium salt*, with $2H_2O$, is deposited in stellate needles or prisms; the *calcium salt*, $C_5H_3BrO_4Ca$ + H_2O, does not crystallise very readily; the *zinc salt* is very characteristic, and may be used to purify the acid; it crystallises from water with $8H_2O$ in colourless prisms; the *silver salt* is deposited in slender needles. All these salts differ from the corresponding bromocitraconates.　　　　　　　　　　　　　　　　　　　　J. B. T.

Solubility of Potassium Hydrogen Tartrate in Alcohol of various strengths. By J. A. ROELOFSEN (*Amer. Chem. J.*, **16**, 464—467).—The following table gives the results obtained.

Milligrams of Potassium Hydrogen Tartrate dissolved in 10 *c.c.*

Temp.	Alcohol, percentage of.									Water.
	90.	80.	70.	60.	50.	40.	30.	20.	10.	
0°	6·2	6·4	4·9	6·0	6·0	6·2	7·0	10·8	17·3	30·1
5	5·5	6·0	5·1	6·0	6·8	6·8	7·1	13·2	18·8	32·0
10	6·2	6·2	5·1	5·8	6·4	7·0	8·6	16·0	27·0	41·1
15	5·3	6·2	6·2	6·2	5·5	7·7	8·8	15·8	23·9	44·3
20	6·4	6·4	6·2	6·4	7·0	9·6	11·3	17·1	29·3	49·0
25	4·7	5·5	6·0	6·8	7·0	10·3	11·7	21·4	36·4	54·1
30	4·7	6·0	6·8	7·5	8·5	11·0	13·1	24·8	39·9	69·2
35	1·9	5·1	5·9	6·8	9·0	12·4	18·8	28·7	49·3	83·8
40	1·7	5·3	5·8	7·0	10·2	14·9	23·1	37·7	53·6	95·9
45	1·7	5·3	6·0	7·9	10·7	16·5	25·8	44·2	72·6	112·8
50	1·5	5·1	6·0	8·1	12·8	19·0	29·7	53 6	87·2	124·8

　　　　　　　　　　　　　　　　　　　　　　　　　　L. T. T.

Dehydromucic acid from δ-Methylpyromucic acid. By H. B. HILL and H. E. SAWYER (*Ber.*, **27**, 1569—1570).—When *w*-methylpyromucic chloride is treated with bromine in sunlight, *w-dibromomethylpyromucic bromide*, $C_6H_3Br_3O_2$, is formed; this crystallises in small, flat prisms, melts at 102°, and is readily soluble in benzene, is readily in cold light petroleum. Hot water converts it into *δ-aldehydopyromucic acid*, $C_6H_4O_4$, which crystallises with $1H_2O$ in long needles. The anhydrous acid forms colourless plates, is readily soluble in alcohol and water, and melts and decomposes at 205°, but may be partially sublimed when carefully heated. It is oxidised by silver oxide to dehydromucic acid, $C_6H_4O_5$, and the same change occurs when its alkaline solution is exposed to the air. *w-Dibromomethylpyromucic acid*, $C_6H_4Br_2O_3$, crystallises in thin tablets melting at 153°. It is difficult to obtain in quantity, and cannot therefore be used for the preparation of the aldehydo-acid.　　　　　　　　A. H.

Succinimide. By E. H. MILLER (*J. Amer. Chem. Soc.*, **16**, 433—462).—The author has obtained succinimide by heating together

ethylene cyanide and acetic acid at 180—200°; by heating together succinic acid and acetonitrile at 180—200°; and by heating together succinic acid and ethylene cyanide in molecular proportion. Determinations of the molecular weight were made by Raoult's method with water, ethylene bromide, and acetic acid as solvents, the average of all the determinations being 99·6, showing the correctness of the generally received formula. The solution gave a very light pink colour with methyl-orange, showing that it is neither strongly acid nor strongly alkaline.

As β-cyanopropionic acid, on heating, should give the unsymmetrical succinimide, the author endeavoured to obtain it by the action of potassium cyanide on potassium β-iodopropionate, and on ethylic β-iodopropionate. Only small quantities of a crystalline and almost neutral compound, $C_8H_{12}N_2O_5$, were obtained. The author believes that β-cyanopropionic acid is an unstable liquid, 2 mols. of which unite with water to form the above compound. This compound crystallises in needles soluble in boiling methyl and ethyl alcohols.

Ethylic β-cyanopropionate, a colourless, odourless liquid boiling at 228° and insoluble in water, was obtained by L. Henry (*Bull. Accad. roy. Belg.*, 1889, **18**, 168). L. T. T.

Acetonitriles. By W. ESCHWEILER (*Annalen*, **279**, 39—44; compare this vol., i, 267).—Aqueous methylamine reacts with methylene-cyanhydrin forming the nitriles of sarcosine and of methyldiglycolamidic acid. The product, when boiled with barium hydroxide solution and the filtrate evaporated with copper oxide, yields the copper derivatives of sarcosine (Strecker, *Annalen*, **157**, 1) and of methyldiglycolamidic acid. The latter crystallises in small, anhydrous, bright blue, four-sided tables.

Methyldiglycolamidic acid, $NMe(CH_2 \cdot COOH)_2$, forms colourless prisms and melts at 226—227° with decomposition. In the reaction between methylamine and methylene cyanhydrin, when a large excess of the former reagent is used, sarcosine nitrile, which cannot be distilled even under diminished pressure without decomposition, is the sole product; whilst, when an excess of methylenecyanhydrin is employed, methyldiglycolamidonitrile only is obtained. The latter boils at 70° under a pressure of 40 mm. If the hydrolysis of the last-named nitrile with barium hydroxide is incomplete, *methyldiglycolamidic acid amide*, $COOH \cdot CH_2 \cdot NMe \cdot CH_2 \cdot CONH_2$, is obtained; it crystallises from aqueous alcohol in long needles, and melts at 168°; the *copper* salt crystallises in deep blue, monhydrated, rhombic prisms, and is sparingly soluble in water.

Dimethylamine reacts very readily with methylene dicyanhydrin, the resulting *nitrile* being an almost odourless liquid, which boils at 137—138°, has a sp. gr. of 0·865 at 20°. When hydrolysed with barium hydroxide, the nitrile yields *dimethylglycocine*, the *copper* derivative of which, $(NMe_2 \cdot CH_2 \cdot COO)_2Cu + 3H_2O$, forms dark blue, rhombic crystals.

Trimethylamine does not react with methylene cyanhydrin.

A. R. L.

Trimethyltrimethylenetrisulphone. By E. LOMNITZ (*Ber.*, **27,** 1667—1679).—Trimethyltrimethylenetrisulphone was prepared by oxidising α-trithioacetaldehyde with permanganate in the presence of sulphuric acid, and from it the potassium, sodium, barium, strontium, and silver salts were prepared. The same was done, starting with β-trithioacetaldehyde. The products were found to be identical in each case. It was hence inferred that only one modification of tri‑methyltrimethylenetrisulphone exists, and, in preparing other deriva‑tives, the trisulphone from either source was indiscriminately used. The trisulphone still contains 3 atoms of displaceable hydrogen; only one of these, it is true, is capable of being displaced by a metal (forming salts that are readily decomposed by carbonic anhydride), but all three can be displaced by alkyl radicles. This is done by adding the iodide or chloride of the radicle to a solution of the tri‑sulphone in caustic soda. In the aliphatic series, the more complex the radicle the less easily can it be introduced; a trimethyl-derivative is formed with ease, but only a little of a triethyl-, with much of a diethyl-derivative can be obtained, and only a little of a triallyl-deriva‑tive, whilst the isobutyl-group cannot be introduced at all. With aromatic radicles, the opposite appears to hold. All 3 hydrogen atoms of the trisulphone can further be displaced by chlorine or bromine, by the direct action of these elements. The formulæ and melting points of the new substances obtained are as follows.

Trimethyltrimethylenetrisulphone, $C_3H_3Me_3S_3O_6$, $(CHMe)_3(SO_2)_3$, or $\begin{array}{c} CHMe \cdot SO_2 \cdot CHMe \\ | \qquad\qquad | \\ SO_2 \cdot CHMe \cdot SO_2 \end{array}$, turns brown at 340°, sublimes at a higher tem‑perature. $C_3H_2Me_3S_3O_6K$. $C_3H_2Me_3S_3O_6Na + 2H_2O$. $(C_3H_2Me_3S_3O_6)_2Ba + 6H_2O$. $(C_3H_2Me_3S_3O_6)_2Sr + 1$ or $6H_2O$. $C_3H_2Me_3S_3O_6Ag + H_2O$. $C_3Me_6S_3O_6$, identical with the product from trimethylenetrisulphone (Abstr., 1890, 26). $C_3Me_3Et_3S_3O_6$, 269°; $C_3HMe_3Et_2S_3O_6$, 239—240°, yields a bromo-derivative, $C_3Me_3Et_2BrS_3O_6$, melting at 221°. $C_3Me_2All_3S_3O_6$, 267°. $C_3Me_3(CH_2Ph)_3S_3O_6$, 268°, yields a trinitro-derivative, decomposing above 132°. $C_3Me_3(CH \cdot C_6H_4Me)_3S_3O_6$, 206°, yields a trinitro-derivative melting with decomposition at 191°. $C_3Me_3Br_3S_3O_6$, 240°; $C_3Me_3Cl_3S_3O_6$, 270°.   C. F. B.

Dithienyls. By K. AUWERS and T. V. BREDT (*Ber.*, **27,** 1741—1747).—The sodium salt of butanetetracarboxylic acid,

$$COOH \cdot CH_2 \cdot CH(COOH) \cdot CH(COOH) \cdot CH_2(COOH)$$
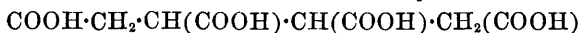
(m. p. 189°), when heated with phosphorus trisulphide yields *ββ-dithi-*
enyl, $\begin{array}{c} CH\!-\!C\!-\!-\!C\!-\!-\!CH \\ \| \quad \| \quad\;\; \| \quad \| \\ CH \cdot S \cdot CH \quad CH \cdot S \cdot CH \end{array}$. This substance has the molecular weight
of 166 in benzene solution, and crystallises in white, lustrous plates, which show a bluish fluorescence and melt at 132°. It is sparingly soluble in glacial acetic acid and light petroleum, more readily in other solvents. Its odour resembles that of naphthalene and also that of some sulphur compounds. It forms a yellow solution in con‑centrated sulphuric acid, and with sulphuric acid and isatin gives a greenish coloration, which becomes brownish-violet on heating. The butanetetracarboxylic acid melting at 236° also yields this substance,

the yield amounting to about 10 per cent. in both cases. Bromine added to a cold solution of the substance in glacial acetic acid probably forms a *dibromo*-derivative, but when the solution is heated a *tetrabromo-ββ-dithienyl*, $C_8H_2Br_4S_2$, is produced. This crystallises in lustrous white needles, melts at 137—138°, and does not give any coloration with sulphuric acid or isatin. *Hexabromo-ββ-dithienyl*, $C_8Br_6S_2$, is formed by the continued action of bromine on a concentrated solution of dithienyl. It separates from benzene in short, compact prisms melting at 183°, and is insoluble in boiling alcohol.

ββ-Dithienyl is isomeric with the *αα*-dithienyl described by Tóhl (this vol , i, 276). This substance forms a *dibromo*-compound which crystallises in large, thin, nacreous plates, melting at 142—143°, and a *tetrabromo*-derivative which crystallises in lustrous needles, and melts at 139—140°. A third dithienyl was obtained by Nahnsen (Abstr , 1884, 1132; 1885, 50) by passing thiophen through a red hot tube. This substance, when submitted to fractional crystallisation and precipitation from glacial acetic acid, yields two compounds, one of which is probably identical with the *ββ*-, the other with *αα*-dithienyl. A. H.

Constitution of Benzene. By A. CLAUS (*J. pr. Chem.*, [2], **49**, 505—524).—A criticism of the recent paper by Brühl (this vol., i, 366) on this subject. The author cannot admit that the evidence adduced in that paper is favourable to Kekulé's formula and at variance with his own formula. A. G. B.

Nitro-derivatives of Tertiary Butylbenzene. By A. BAUR (*Ber.*, **27**, 1610—1611).—By the action of nitric acid (sp. gr. 1·48) on tertiary butylbenzene at low temperatures *nitrobutylbenzene*, $C_{10}H_{13}·NO_2$, is formed, it is a viscid liquid, volatile with steam, and has a highly unpleasant smell. On warming with fuming nitric acid it is converted into the *dinitro-derivative*, $C_{10}H_{12}(NO_2)_2$, which is deposited from alcohol in yellow crystals melting at 61—62°. The *trinitro-derivative*, $C_{10}H_{11}(NO_2)_3$, is formed by the action of nitrosulphuric acid on dinitrobutylbenzene, and crystallises in pale yellow needles, melting at 108—109°. None of these compounds smell of musk. J. B. T.

Dinitrobutyltoluene. By A. BAUR (*Ber.*, **27**, 1624).—In a previous communication on artificial musk (Abstr., 1891, 1464), dinitrobutyltoluene was described as a viscid liquid. After several months it has crystallised in small, pale yellow needles melting at 92°.

J. B. T.

Bromobutyltoluene. By A. BAUR (*Ber.*, **27**, 1619—1623).—*Bromobutyltoluene*, $C_4H_9·C_6H_3BrMe$ [Me : C_4H_9 : Br = 1 : 3 : 6], is prepared by the action of bromine on butyltoluenesulphonic acid, or on the sodium salt at 50—60°; it is an almost colourless liquid, boiling at 240—242°, and has an aromatic smell. The *dinitro-derivative* is liquid, has a characteristic pungent odour, and could not be converted into a trinitro-compound. By the action of bromine on butyltoluene a

bromo-derivative is formed, which boils at 238—242°, and may be identical with the bromobutyltoluene prepared from the sulphonic acid. On treatment with nitric acid, two compounds are formed, the one, $C_4H_9 \cdot C_6H_2BrMe \cdot NO_2$, is a pale yellow liquid which volatilises with steam, readily decomposes when distilled, and darkens on exposure to air. The second, $C_4H_9 \cdot C_6HBrMe(NO_2)_2$, crystallises from alcohol in yellow needles melting at 107—108°. Neither of these substances smells of musk. By the action of bromine on butyltoluenesulphonic acids, or the sodium salt, at 20—30° the *bromosulphonic acid* is formed and crystallises in colourless, lustrous plates. The *sodium* and *lead salts* are crystalline. On treatment with nitric acid, it is converted into trinitrobutyltoluene and *butyltoluenenitrobromosulphonic acid*, which is soluble in water and is being further investigated. J. B. T.

Bye-Products formed in the Preparation of Butyltoluene.

By A. BAUR (*Ber.*, **27**, 1606—1609).—An examination of the various fractions obtained during the purification of butyltoluene (Abstr., 1891, 1464), shows that the portion boiling at 160—180° consists chiefly of butylbenzene (b. p. 167°).

The fraction 180—190° contains a little butylxylene, although the greater portion is butyltoluene; butylxylene is also contained in the fractions 190—200° and 200—218°. Tertiary butylxylene, which boils at 202°, is readily sulphonated; the *sodium salt* crystallises in lustrous plates, the sulphonamide in pearly plates melting at 141—142°, whilst the sulphanilide forms colourless needles melting at 143—144°.

The fraction 220—250° contains two hydrocarbons; the one is tertiary dibutylbenzene, and crystallises in colourless prisms melting at 76°; the *dinitro-derivative*, $C_{14}H_{20}(NO_2)_2$, crystallises in colourless needles, melts at 167—168°, and has a faint odour of musk. A trinitro-compound could not be obtained. *Barium dibutylbenzenesulphonate*, $2(C_{14}H_{21} \cdot SO_3)_2Ba + 7H_2O$, crystallises in colourless plates. The liquid hydrocarbon boils at 240—245°, and is *dibutyltoluene ;* the *trinitro-derivative*, $C_{15}H_{21}(NO_2)_3$, crystallises in colourless plates, melts at 152—153°, and has a faint odour of musk. Both dibutylbenzene and dibutyltoluene were prepared, for purposes of comparison, directly from benzene, isobutylic bromide or pseudobutylic chloride, and aluminium chloride.

The fraction boiling above 250° after purification appears to consist of tributylbenzene and tributyltoluene, and is being further investigated. J. B. T.

Ethylbutylbenzene.

By A. BAUR (*Ber.*, **27**, 1611—1614).—Ethylbutylbenzene is readily prepared by the action of ferric chloride on a mixture of pseudobutylic chloride and ethylbenzene at about 10°; it boils at 205—206°, and the yield is 73 grams from 200 grams of ethylbenzene. At higher temperatures or in presence of aluminium chloride the reaction is much more complicated. *Sodium ethylbutylbenzenesulphonate* crystallises in colourless, lustrous plates. The *sulphonamide*, $C_{12}H_{17} \cdot SO_2 \cdot NH_2$, is deposited from alcohol in plates melting at

98°. The *disulphonamide*, $C_{12}H_{16}(SO_2\cdot NH_2)_2$, and the *disulphonic chloride* are crystalline, the former melts at 228—229°. The *dinitro-derivative*, $C_{12}H_{16}(NO_2)_2$, crystallises in pale yellow needles, melts at 140°, and has a faint odour of musk. The *trinitro-product* was only obtained on one occasion; it smells strongly of musk, is readily soluble in alcohol, and crystallises with difficulty. J. B. T.

Stability of Iodoso-compounds at Ordinary Temperatures.

By C. WILLGERODT (*Ber.*, **27**, 1826—1827).—A sample of iodosobenzene, after being at the Chicago Exhibition, appeared unchanged, but, on treatment with chloroform, proved to have decomposed completely into iodobenzene and iodoxybenzene; another specimen which had been kept on paper, under a watch-glass, for about a year, became white and decomposed in a similar manner. Under the same conditions, metanitroiodosobenzene and orthochloriodosobenzene were completely decomposed into the corresponding iodoxy- and iodo-derivatives; parabromiodosobenzene was scarcely changed, whilst parachloriodobenzene acetate was converted into the iodoso-compound. J. B. T.

Idodoso- and Iodoxy-derivatives of Paradiiodobenzene.

By C. WILLGERODT (*Ber.*, **27**, 1790—1794).—*Diiodobenzene dichloride*, $C_6H_4I_2Cl_2$, is obtained by passing chlorine into a chloroform solution of paradiiodobenzene, until a considerable quantity of the dichloride is precipitated. In crystallises in beautiful, short, yellow prisms, and decomposes at 150°. When dissolved in alcohol, acetone, or acetic acid it is completely decomposed into paradiiodobenzene.

Paraiodosoiodobenzene, $C_6H_4I\cdot IO$, obtained by treating the dichloride with sodium hydroxide, is an amorphous, bright, yellow powder, and explodes at 120°. When boiled with water, it is converted into iodoxyiodobenzene and paraiodobenzene, and when boiled with alcohol into paraiodobenzene.

Paraiodophenyliodoacetate, $C_6H_4I\cdot I(OAc)_2$, is obtained by rubbing the preceding compound with cold acetic acid. It crystallises in transparent plates, and melts at 215°. When paraiodosoiodobenzene is dissolved in boiling acetic acid, paradiiodobenzene, the acetate, and a compound which melts at 210—225° are obtained; the latter is probably impure paradiiodobenzene.

Paraiodoxyiodobenzene, $C_6H_4I\cdot IO_2$, is obtained, either by boiling iodosoiodobenzene with water, or by heating it in a current of steam at 90—100°. It crystallises in white needles, and explodes with a loud report at 232°.

Diiodobenzene tetrachloride, $C_6H_4(ICl_2)_2$, is obtained in a pure state from paradiiodobenzene dichloride and chlorine. It crystallises in bright, yellow needles, and decomposes at 157—159° (Abstr., 1893, i, 149).

Paradiiodosobenzene, isomeric with iodoxyiodobenzene, is a bright, yellow powder, and when heated decomposes without explosion.

Paraphenylene diodide tetracetate, $C_6H_4[I(OAc)_2]_2$, is obtained by boiling the preceding compound with acetic acid. It crystallises in small prisms, and decomposes and melts at 232°.

Paradiiodoxybenzene, $C_6H_4(IO_2)_2$, is obtained by boiling diiodoso-benzene with water. It crystallises in white, microscopic needles.

E. C. R.

Diphenylic Selenide and its Derivatives. By F. KRAFFT and R. E. LYONS (*Ber.*, **27**, 1761—1768; Abstr., 1894, i, 88).—Diphenylic selenide, obtained by the method already described by the author), boils at 159° under 10 mm., at 163° under 14 mm., at 167° under 16·5 mm., at 199° under 55 mm., at 219° under 100 mm., and at 227° under 126 mm. pressure. It is decomposed when heated with strong nitric acid, but dissolves in cold nitric acid (sp. gr. = 1·4) to form the nitrate of diphenylic selenoxide, which, on the addition of hydrochloric acid, is converted into the dichloride, Ph_2SeCl_2 (m. p. 182°).

Diphenylic diselenide, Se_2Ph_2, is obtained from diphenylic selenide by a method similar to that by which phenylic disulphide is obtained from phenylic sulphide, namely, by warming the selenide with selenium. It crystallises in yellow needles, melts at 63·5°, and distils at 202—203° under 11 mm. pressure, with slight decomposition. When distilled under the ordinary pressure, either alone or dissolved in alcohol, it is decomposed into phenylic selenide and selenium.

Phenylic hydroselenide, SeHPh, is obtained by reducing the diselenide with sodium and alcohol, acidifying the product with sulphuric acid, and subjecting it to steam distillation. It is a colourless, highly refractive oil, boils at 183°, and oxidises, on exposure to air, to form the diselenide. The specific gravity at 0° = 1·5057, at 15° = 1·4865. It gives yellowish-red, unstable precipitates with alcoholic silver and lead solutions.

Dichlorophenylic selenide, $Se(C_6H_4Cl)_2$, is obtained, together with phenyl selenide, by heating the dichloride, Ph_2SeCl_2, first at 140—150°, and then at 170—180°. It crystallises in lustrous leaflets, and melts at 95—96°.

Dibromophenylic selenide, $Se(C_6H_4Br)_2$, is obtained in a similar way to the chloro-compound, or by heating diphenylic selenide with bromine at 140°. It crystallises in lustrous, hexagonal leaflets, and melts at 115·5°.

β-Dinaphthylic selenide, $Se(C_{10}H_7)_2$, is obtained by heating β-di-naphthylsulphone with selenium. It boils at 298° under 12 mm. pressure, melts at 138·5°, and forms with bromine the orange-red *dibromide*, $SeBr_2(C_{10}H_7)_2$, which when treated with alkalis is reconverted into the selenide. E. C. R.

Diphenylic Telluride and the Preparation of Sulphides, Selenides, and Tellurides. By F. KRAFFT and R. E. LYONS (*Ber.*, **27**, 1768—1773).—When mercury diphenyl, $HgPh_2$, is heated with tellurium dichloride at 220—225°, monochlorobenzene, and mercury telluride are formed.

Diphenylic telluride, $TePh_2$, is obtained by heating mercurodiphenyl with tellurium in an atmosphere of carbonic anhydride at 220°. It is a clear oil, which boils at 174° under 10 mm., and at 182—183° under 16·5 mm. pressure, whilst under ordinary pressures it decomposes,

yielding benzene and a crystalline solid. The sp. gr. at $0° = 1·5741$, and at $15·2° = 1·5558$.

Phenylic telluride dibromide, $TeBr_2Ph_2$, is obtained by adding bromine to an ethereal solution of the telluride. It crystallises in small, lustrous prisms, melts at $203·5°$, and is very similar to the selenium compound. When warmed with a solution of sodium hydroxide at $50°$, it is converted into *phenylic telluroxide*, $TePh_2O$, which crystallises in needles, and melts at $185°$ with decomposition.

Mercury diphenyl, when heated with selenium and sulphur at $220-230°$, is converted respectively into diphenylic selenide and sulphide. And this method is a very convenient one for the preparation of these and similar compounds.

Finally, the authors give tables showing the great similarity of the sulphur, selenium, and tellurium compounds.   E. C. R.

Melting Points of some Phenols and their Benzoates. By A. BÉHAL and E. CHOAY (*Compt. rend.*, **118**, 1211—1213).—The authors have prepared synthetically, by diazotisation of the corresponding amines, the phenols which, from their boiling point, might exist in officinal cresote. The benzoates were obtained by the action of benzoic chloride on a solution of the phenol in excess of sodium hydroxide solution. With the exception of the orthocresyl compound, which is liquid, the benzoates are all crystalline solids, very soluble in most organic solvents, but insoluble in water. The melting points and boiling points of the phenols were found to be as follows:—
Phenol, m. p. $42·5-43$, b. p. $178·5°$; orthocresol, m. p. $30°$, b. p. $178·5°$; metacresol, m. p. $4°$, b. p. $200°$; paracresol, m. p. $36·5°$, b. p. $199°$; orthoethylphenol (liquid), b. p. $202-203°$; metaethylphenol, m. p. $-4°$, b. p. $214°$; paraethylphenol, m. p. $45-46°$, b. p. $218·5-219°$; ortho-xylenol [1 : 2 : 3], m. p. $73°$, b. p. $212-213°$; ortho-xylenol [1 : 2 : 4], m. p. $65°$; b. p. $222°$; paraxylenol, m. p. $75°$, b. p. $208-209°$; metaxylenol [1 : 3 : 4], m. p. $25°$, b. p. $208-209°$.

For the corresponding benzoates, the values are:—Phenyl, m. p. $69°$, b p. $298-299°$; orthocresyl (liquid), b. p. $307°$; metacresyl, m. p. $54°$, b. p. $313-314°$; paracresyl, m. p. $71·5°$, b. p. $315·5-316°$; orthoethylphenyl, m. p. $38°$, b. p. $314-315°$; metaethylphenyl, m. p. $52°$, b. p. $322-323°$; paraethylphenyl, m. p. $59-60°$, b. p. $328°$; ortho-xylyl [1 : 2 : 3], m. p. $58°$, b. p $326-327°$; ortho-xylyl [1 : 2 : 4], m. p. $58·5°$, b. p. $333°$; paraxylyl, m. p. $61°$, b. p. $318-319°$, metaxylyl [1 : 3 : 4], m. p. $38·5°$, b. p. $321°$; metaxylyl [1 : 3 : 5], m. p. $24°$, b. p. $326°$.

In some cases, the results agree with, but in others they differ considerably from, those of previous observers. The authors have not yet succeeded in obtaining the metaxylenol [1 : 2 : 3] and its derivatives described by Greving.   C. H. B.

Phenols and Ethers of Butyltoluene. By A. BAUR (*Ber.*, **27**, 1614—1619).—*Trinitrobutylorthocresol*, $C_4H_9·C_6Me(NO_2)_3·OH$, is prepared by the action of nitric acid on butylorthocresol (b. p. $235-237°$) at low temperatures, and crystallises from alcohol in yellow needles melting at $85-86°$. From the *silver salt*, which crystallises in brown needles, the *methoxy-derivative*, $C_4H_9·C_6Me(NO_2)_3·OMe$, was

obtained; this is deposited in yellowish needles, melts at 69—70°, and has an odour of musk. It is also formed by nitrating butyl-orthomethoxytoluene. That the above compounds contain a tertiary butyl group is shown by the preparation of the phenol, by the action of zinc chloride on a mixture of cresol and isobutylic alcohol or pseudo-butylic chloride; the same phenol is also formed on fusing sodium metabutyltoluenesulphonate with potash. Butylmetacresol and butylparacresol resemble the ortho-derivative, and boil at about the same temperature, the *nitro-compounds* crystallise with great difficulty, and have the odour of musk. The *methoxy-derivatives* are oily.

Butylmetamethoxytoluene, which boils at 222—224°, is nitrated with difficulty, as the butyl group is readily eliminated, and trinitrometa-methoxytoluene formed. The propoxy- and amyloxy-compounds decompose in a similar manner. By the action of nitric acid on butylmetamethoxytoluene in glacial acetic acid solution at the ordinary temperature, a mixture of the *di-* and *trinitro*-compounds is formed; the former is oily and has a disagreeable odour, the latter crystallises in pale yellow plates, has an odour of musk, and darkens on exposure to light; the specimen was not quite pure. Attempts to determine the constitution of the butylmethoxytoluenes by oxidation with chromic anhydride or potassium permanganate were unsuccessful.

Butylmethoxybenzene, prepared by the action of aluminium chloride on methoxybenzene and isobutylic bromide or pseudobutylic chloride, has an aromatic odour, and boils at 220—222°. The *dinitro-derivative*, $C_4H_9 \cdot C_6H_2(NO_2)_2 \cdot OMe$, crystallises in lustrous, yellow plates, and melts at 100—101°. The *trinitro-derivative*, $C_4H_9 \cdot C_6H(NO_2)_3 \cdot OMe$, is deposited from alcohol in yellow needles melting at 74—75°. Neither of them has any odour of musk.   J. B. T.

Preparation of Aniline. By A. Wohl (*Ber.*, **27**, 1815—1818).— When writing his previous paper (this vol., i, 409), the author was unaware that in 1887 O. N. Witt suggested that in the preparation of naphthylamine ferrous chloride is the real reducing agent, and that the action takes place in accordance with the equations:—(I) $6FeCl_2 + C_{10}H_7 \cdot NO_2 + H_2O = 3Fe_2Cl_4O + C_{10}H_7 \cdot NH_2$; (II) $4Fe_2Cl_4O + 3Fe = Fe_3O_4 + 8FeCl_2$. Against this it is urged that the presence of other salts, such as calcium chloride, which have no reducing action, greatly facilitate the transference of oxygen from the nitro-compound to the iron, and that extremely concentrated solutions of ferrous salts, in absence of alkalis, have little action on nitrobenzene, and none, when the solutions are of the same strength as are employed technically. In the author's opinion the reduction is caused by the finely divided moist metal. Recently prepared ferric hydr-oxide, like basic ferric chloride, in presence of ferrous chloride, is converted into ferrosoferric oxide by the action of finely-divided iron. Witt's second equation is, therefore, correct. In a footnote it is pointed out that dilute, aqueous solutions of nitrobenzene have a remarkably sweet taste.   J. B. T.

Action of Ammonia and Primary Amines on Orthohydroxy-benzylic Alcohol. By C. Paal and H. Senninger (*Ber.*, **27**, 1799—

1804).—Orthodihydroxybenzylamine is formed by the interaction of orthohydroxybenzylic alcohol and alcoholic ammonia at 140—145°; the yield is 40—50 per cent. of the theoretical, and a considerable quantity of the unaltered alcohol may be recovered. The compound gives a reddish-brown coloration and precipitate with sodium nitrite in acid solution. The hydrochloride, $C_{14}H_{15}NO_2,HCl$, gives a violet colour with ferric chloride, and melts at 190° instead of 144° as stated by Emmerich. Hydroxysalicylamide melts at 156° instead of 145°. *Saliretazine*, $C_{35}H_{33}O_5N$, is obtained in small quantity with orthodihydroxybenzylamine, and is the sole product of the action at 180—200°; it forms intensely yellow crystals, is insoluble, and decomposes above 300° without melting. The base is not decomposed by heating with alcoholic hydrochloric acid, concentrated sulphuric acid, or fuming nitric acid. The *hydrochloride* is colourless and insoluble. Orthohydroxybenzylaniline is prepared by the action of aniline on orthohydroxybenzylic alcohol, and has been previously obtained by O. Fischer and Emmerich (*Annalen*, **241**, 343); the *sodium salt*, $NHPh \cdot CH_2 \cdot C_6H_4 \cdot ONa$, crystallises in silky, lustrous needles, and readily dissociates. The *nitrosamine* is a reddish-yellow, viscid liquid, which decomposes spontaneously. The *acetyl* derivative crystallises in long, colourless plates, melting at 96°. Orthohydroxybenzylparatoluidine, $C_6H_4Me \cdot NH \cdot CH_2 \cdot C_6H_4 \cdot OH$, is formed from paratoluidine and orthohydroxybenzylic alcohol. The yield is almost quantitative.

J. B. T.

Condensation Products of Aromatic Amines with Formaldehyde in Alkaline Solution. By C. Aberhardt and A. Welter (*Ber.*, **27**, 1804—1815).—*Methylenediphenyldiimide*, $CH_2(NHPh)_2$, is prepared by the interaction of aniline, formaldehyde, and potassium hydroxide in alcoholic solution at 100°; the yield is almost quantitative. It is also formed from formanilide and formaldehyde, and from anhydroformaldehydeaniline and aniline, and is probably identical with a compound obtained by Lermontoff from methylenic iodide and aniline, and with one (m. p. 48—49°) obtained in small quantity about nine years ago by Pratesi from aniline and formaldehyde. The base crystallises in large, lustrous, quadratic plates, melts at 64—65°, and boils and slightly decomposes at about 209—210°. It volatilises with steam but at the same time decomposes; on boiling with alcohol, it is resolved into anhydroformaldehydeaniline and a polymeric compound which crystallises in quadratic plates, and melts at 192°. On boiling with dilute sulphuric acid, both compounds yield formaldehyde.

Methylenediorthotolyldiimide, $CH_2(NH \cdot C_6H_4Me)_2$, is prepared in a manner similar to the phenyl-derivative, and crystallises in colourless prismatic needles melting at 52°. Anhydroformaldehydeorthotoluidine is not an oil as Tollens states, but crystallises in lustrous plates, and melts at about 100°. *Methylenediparatolyldiimide* is obtained like the ortho-derivative, and crystallises in silvery, lustrous plates melting at 86°; it is comparatively stable, can be recrystallised from alcohol, and dissolves in dilute mineral acids. Anhydroformaldehydeparatoluidine exists in two modifications, melting at 123° and 207—209° respectively. The quantity of alkali employed has little

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influence on the above condensations; potash acts better than soda; ammonia has no action.

By the action of hydrochloric acid or of amine hydrochlorides, the above imides are converted into diamidodiphenylmethane-derivatives. Diamidodiphenylmethane is deposited from water in lustrous plates or needles, and from benzene in prisms, melting at 88—89°. The *hydrochloride* crystallises in needles, it melts and darkens above 285°, and in aqueous solution exhibits a yellowish-green fluorescence. The *diacetyl-derivative* is crystalline, and melts at 228°. The *sulphonic acid* resembles that of diamidodiorthotolylmethane (see below); the *barium, potassium*, and *sodium salts* are crystalline. In addition to the methods already described, *diamidodiorthotolylmethane*,

$$CH_2(C_6H_3Me \cdot NH_2)_2,$$

is formed by the action of hydrogen chloride on the diimide at −15°, also by heating methylenediphenyldiimide or methylenediparatolyl-diimide with orthotoluidine hydrochloride. The *acetyl-derivative* melts at 198°. The *nitro-derivative* is yellow and sparingly soluble. The *hydrochloride* forms lustrous needles, melting at 278° with de-composition. The *disulphonic acid*, $C_{15}H_{16}N_2(SO_3H)_2$, crystallises in dark green, sparingly soluble needles. With nitrous acid, a blue coloration is obtained changing successively to reddish-violet and dirty brown; the reaction is extremely delicate. The *ammonium* and *potassium salts* are crystalline.

Diamidophenyltolylmethane, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3Me \cdot NH_2$, is prepared by heating a mixture of methylenediorthotolyldiimide, aniline, and aniline hydrochloride in molecular proportion; it crystallises in lustrous plates, and melts at 129°. The *hydrochloride* and *sulphate* are readily soluble. *Diamidoditolylmethane*, $CH_2(C_6H_3Me \cdot NH_2)_2$ [Me : NH_2 : CH_2 = 1 : 4 : 5], is prepared from methylenediparatolyldiimide and paratoluidine hydrochloride, and crystallises in colourless, silky needles, melting at 92°. The *sulphate* is readily soluble in water, and the *hydrochloride* sparingly so, with a yellowish-green fluorescence.

Dihydroxydiphenylmethane, $CH_2(C_6H_4 \cdot OH)_2$, is prepared from the diamido-compound by the diazo-reaction; it crystallises in lustrous plates or needles, and is readily soluble in alkalis. The *potassium salt* crystallises in needles. *Paradihydroxydiorthotolylmethane*, $CH_2(C_6H_3Me \cdot OH)_2$, is prepared in a similar manner, and is deposited in lustrous needles or plates melting at 126°. The *alkali salts* are readily soluble.

Methylenediphenyldiimide is converted into pararosaniline by heat-ing it with aniline hydrochloride and aniline in presence of iron and an oxidising agent. Methylenediorthotolyldiimide acts in a similar manner yielding *triamidotritolylmethane*, which is crystalline, and melts and decomposes at 155—160°. The *triacetyl-derivative* crystal-lises in small needles, melting at 170°. *Triamidotriorthotolyl carbinol hydrochloride* forms long, green needles, and is tolerably stable to-wards acids.   J. B. T.

Properties and Hydrolysis of Isomeric Amidines. By H. v. PECHMANN (*Ber.*, **27**, 1699—1702).—*Benzenylphenylamidoparatolyl-*

imidine, NHPh·CPh:N·C₆H₄Me, was prepared by acting on benzo-paratoluidide with phosphoric chloride, and treating the product with aniline; it melts at 133°. *Benzenylparatolylamidophenylimidine.* C₆H₄Me·NH·CPh:NPh, obtained by the successive action of phosphoric chloride and paratoluidine on benzanilide, melts at 128°. These two substances cannot be distinguished from each other in appearance, and, when hydrolysed by boiling with water or dilute acid, the first does not yield, as would be expected, a mixture of benzanilide and paratoluidine, nor the second a mixture of benzoparatoluidide and aniline; but each yields a mixture of all these four substances. It may be supposed that a molecule of water is first taken up, and that the compound thus formed decomposes in two different ways.

C. F. B.

Action of Nascent Bromine on Benzene Derivatives. By W. VAUBEL (*J. pr. Chem.*, [2], **49**, 540—545).—The author reviews the action of bromine on azobenzene, hydrazobenzene, diazobenzene, phenylhydrazine, acetylphenylhydrazine, benzamide, benzoic acid and its nitro-derivatives, and discusses the influence which the characteristic groups of these compounds exert on the position assumed by the bromine entering into the compounds (compare Abstr., 1893, i, 560; this vol., i, 19). A. G. B.

Stereoisomerism of the Diazo-compounds; Constitution of Isodiazo-compounds. By A. HANTZSCH (*Ber.*, **27**, 1702—1725; compare the two following abstracts).—The isodiazo-compounds have hitherto been regarded as structurally isomeric with the diazo-compounds, the iso-compounds being looked on as nitrosamines, such as isodiazobenzene, NHPh·NO. The evidence on which this formula principally rests is the fact that when the potassium salts of the isodiazo-compounds are treated with alkyl iodides, the nitrosamines of the secondary bases are produced, isodiazobenzene and methylic iodide, for example, yielding methylphenylnitrosamine, identical with that obtained from methylaniline. Against this view may be urged that the silver salts, on the other hand, yield chiefly the oxygen ethers, such as nitrodiazobenzene methyl ether, C₆H₄NO₂·N:N·OMe, and that the acid derivatives of the isodiazo-compounds, when hydrolysed in alkaline solution, yield true diazo-compounds, in spite of the fact that it is precisely in alkaline solution that the iso-compounds are most stable. The formation of "nitrogen"- or "oxygen"-ethers by the action of alkyl iodides on metallic derivatives cannot be used as evidence for the constitution of a compound, as is shown by the well-known case of the stereoisomeric oximes, and all that can be legitimately concluded from these facts is, that the diazo-compounds are tautomeric and may react either in the sense of a true diazo-compound or of a nitrosamine. That the diazo- and isodiazo-compounds have the *same* structural formula is proved by the following facts:—Two isomeric diazoamidobenzenes exist, and the structure of these cannot be explained by the nitrosamine formula. The newly discovered isomeride, which will form the subject of a separate communication, differs from the one already known in being explosive and in possessing the property of forming colouring matters directly.

If the nitrosamine formula were accepted, these isomeric substances would have the formulæ (1) NPh:N·NHPh derived from NPh:N·OH, and (2) NHPh·N:NPh derived from NHPh·NO, and it will be seen that these formulæ are not different but identical.

Further (see the following abstract) the salts of benzenediazo-sulphonic acid exist in two isomeric forms, one of which passes spontaneously into the other in aqueous solution, a change which would necessitate a complex intramolecular change were the nitros-amine formula to be accepted.

The actual relation between the diazo- and isodiazo-compounds can in fact only be consistently expressed by regarding these sub-stances as stereochemically isomeric, in the same manner as the isomeric oximes. These substances will then be represented by the formulæ

$$\begin{array}{cc} \text{Ph·N} & \text{Ph·N} \\ \text{X·N} & \text{N·X} \end{array}$$

Syndiazo-compounds.   Antidiazo-compounds.
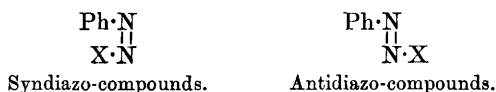
which differ from the formulæ of the oximes only by the substitution of N for the group CH.

Such diazo-compounds as exist in the form of rings, due to the formation of inner anhydrides (as, for example, the anhydrides of diazobenzensulphonic acid and of nitrodiazophenol) must be syn-compounds, and, as these, as well as all ordinary diazo-compounds, react with phenols to produce colouring matters, this property may be taken as characteristic of the syn-series. In alkaline solution, these syn-compounds gradually change into the anti-compounds, and these do not form azo-colouring matters. This is confirmed by the fact that the syn-compounds tend to decompose with evolution of nitrogen, whilst the anti-compounds yield two molecules, each con-taining one of the diazo-nitrogen atoms. These decompositions are quite in accordance with the corresponding changes of the stereo-isomeric oximes. Finally, the syn-compounds are characterised by a tendency to explode, which is absent from the anti-compounds.

Among the syn-diazo-compounds are comprised the diazo-salts, and a new diazoamidobenzene and potassium benzenediazosulphonate, whilst the "isodiazo-compounds," the well-known diazoamido-com-pounds, and the stable potassium benzenediazosulphonate belong to the anti-series; antidiazo-salts of the mineral acids are not yet known. The replacement of X in a syn-diazo-compound of the formula $\begin{array}{c}\text{Ph·N}\\\text{X·N}\end{array}$ by a more positive group renders the compound less stable, and more liable to spontaneous change into the corresponding anti-compound, whilst, inversely, when the group X of an anti-com-pound is replaced by a more negative group the compound tends to change into the syn-derivative. It must be remembered that syn-diazobenzene corresponds with synbenz-anti-aldoxime, $\begin{array}{c}\text{Ph·C·H}\\\text{HO·N}\end{array}$, and antidiazobenzene with antibenz-syn-aldoxime, $\begin{array}{c}\text{Ph·C·H}\\\text{N·OH}\end{array}$. The use of

the contracted terms anti-aldoxime and syn-aldoxime entirely destroys
the analogy. A. H.

Stereoisomeric Salts of Benzenediazosulphonic acid. By A.
HANTZSCH (*Ber.*, **27**, 1726—1729; compare foregoing abstract). The
acid of the constitution $PhN:N\cdot SO_3H$, which is usually termed diazo-
benzenesulphonic acid, is more correctly designated as benzenediazo-
sulphonic acid. Its salts exist in two stereoisomeric forms.

Potassium benzenesyndiazosulphonate, $\begin{smallmatrix} Ph\cdot N \\ \parallel \\ SO_3K\cdot N \end{smallmatrix}$, may be obtained by

bringing a solution of diazobenzene nitrate into an ice-cold solution
of neutral potassium sulphite containing an excess of potassium
carbonate. The salt is precipitated as a reddish-yellow crystalline
mass, which is rapidly collected, washed once or twice with ice-cold
water, and then dried on a porous plate. It forms a deep orange-
coloured mass of plates, containing $1H_2O$; it rapidly loses water
in the air, and then immediately begins to decompose, the colour
becoming brownish, and finally dark brown, and sulphurous anhy-
dride being evolved. The salt very frequently takes fire and explodes
as soon as it becomes dry. It can nevertheless be analysed by
exposing it over phosphoric oxide for a few minutes. This salt is a
true derivative of diazobenzene nitrate (syn-series), as is shown by
the liability to decomposition and by the fact that phenol is formed
when it is boiled with water, and that it reacts with alkaline solutions
of phenols to form coloured azo-compounds.

Potassium benzeneantidiazosulphonate, $\begin{smallmatrix} Ph\cdot N \\ \parallel \\ N\cdot SO_3K \end{smallmatrix}$, is the salt

which is familiar from the descriptions of Strecker, E. Fischer,
and Paal. The clear, dark yellow solution of the syn-salt be-
comes much lighter at the ordinary temperature, and the anti-salt
soon separates out in granular crystals. It is pale yellow, is
much less soluble than the syn-compound, and does not react
with phenols to form coloured substances. Boiling water appa-
rently produces much less phenol than with the syn-salt. The
two salts behave similarly to reducing agents, with the exception
that the reduction of the syn-salt is always accompanied by a slight
evolution of nitrogen, which is never the case with the anti-salt.
The syn-compound, moreover, is always partially converted into resin
by bromine water, whilst this does not occur with the anti-salt.

The other salts of benzenediazosulphonic acid also exist in two
forms. Thus the *barium salt* of the syn-acid rapidly separates as a
yellow microcrystalline powder, which forms a clear solution in
hydrochloric acid, whilst barium chloride produces no precipitate in
a solution of the potassium salt of the anti-acid. The *silver* salt of
the anti-series crystallises remarkably finely, forming yellow lustrous
needles. Salts of silver and lead produce white precipitates of the
sulphites of the metals with a solution of the syn-potassium salt,
diazobenzene nitrate being quantitatively regenerated according to
the equation $Ph\cdot N_2\cdot SO_3K + 2AgNO_3 = Ag_2SO_3 + KNO_3 + Ph\cdot N_2\cdot NO_3$.

Copper sulphate only produces a green coloration with the anti-potassium salt, whilst with the syn-salt a rapid and apparently quantitative evolution of nitrogen is produced, so that this salt, like the other syn-derivatives, undergoes Sandmeyer's reaction.

A. H.

Constitution of Benzenediazoic acid. By A. HANTZSCH (*Ber.*, **27**, 1729—1731).—Benzenediazoic acid (phenylnitramine), which is a derivative of isodiazobenzene, probably has the constitution $Ph \cdot N \underset{N-OH}{\overset{|}{>}} O$, and is therefore to be looked upon as an oxidised antidiazo-benzenehydrate. Like isodiazobenzene itself, it is a tautomeric substance, and sometimes acts as though it had the constitution $Ph \cdot NH \cdot NO_2$ assigned to it by Bamberger; this, for instance, is the case when the potassium salt is acted on with methylic iodide, the "nitrogen-ether" being the chief product, whereas the silver salt yields the "oxygen-ether."

Similar considerations hold for naphthalenediazoic acid.

A. H.

Mixed Formazyl-compounds. By H. v. PECHMANN (*Ber.*, **27**, 1679—1693).—The formation of a formazyl-derivative by the action of a diazo-compound on a hydrazone is, to take a particular case, represented by the equation $N_2HPh \colon CHPh + OH \cdot N_2Ph = H_2O + N_2HPh \colon CPh \cdot N_2Ph$. Since the hydrogen of the imido-group in the hydrazone takes no part in the reaction, it might appear that formazyl-compounds could be equally well prepared from hydrazones in which some other group was substituted for this hydrogen. Curiously enough, this is not the case. Nor is this the only peculiarity of the hydrogen atom in question. Formazyl-compounds of the types $N_2HX \colon CR \cdot N_2Y$ and $N_2HY \colon CR \cdot N_2X$ ($R = H$, $COOH$, Ph, or N_2Ph), exhibit so close a similarity that it might be supposed that structurally they are not merely isomeric, but identical, the position of the hydrogen atom being immaterial. As a rule, two corresponding compounds of this type have precisely the same appearance, and identical, or nearly identical, melting points; and, in chemical reactions, each compound yields, not only the products that it would be expected to form, but also those that would be expected from the other, or, in one case, both compounds give the products that would be expected from one only of the two. However, the author, chiefly on the ground that isomeric mixed amidines exhibit the same similarity whilst their melting-points differ by as much as 5° (this vol., i, 452), considers that these compounds are truly isomeric, and that their anomalous chemical behaviour is due to the fact that each is partially converted into its isomeride by most chemical reagents. He sees a similar isomerism in the case of mixed diazo-amido-compounds of the types $NHX \cdot N \colon NY$ and $NHY \cdot N \colon NX$, and of mixed amidines of the types $NHX \cdot CR \colon NY$ and $NHY \cdot CR \colon NX$.

Ethylic h-phenyl-a-paratolylformazylformate (see Abstr., 1893, i, p. 85) was prepared from paradiazotoluene and the phenylhydrazone either of ethylic hydrogen mesoxalate, or of ethylic acetacetate; it is red, and melts at 85°. The *acid*, $N_2HPh \colon C(COOH) \cdot N_2 \cdot C_6H_4Me$, is

brownish-red, and melts at 164—165°. When treated with diazo-benzene, it yields *benzeneazo-h-phenyl-a-paratolylformazyl*,

$$N_2HPh\dot{:}C(N_2Ph)\cdot N_2\cdot C_6H_4Me,$$
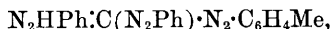
which can also be prepared from formazylformic acid and para-diazotoluene; it is red, with a bronze lustre, and melts at 174—175°.

Methylic h-paratolyl-a-phenylformazylformate was prepared from diazobenzene and the paratolylhydrazone of methylic acetoacetate (yellow needles, melting at 100°, prepared from paradiazotoluene and methylic acetoacetate); it is red, and melts at 98°. The *acid*,

$$C_6H_4Me\cdot N_2H\dot{:}C(COOH)\cdot N_2Ph,$$
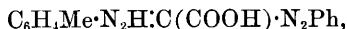
is red, and melts at 165—166°. When treated with diazobenzene, it yields *benzeneazo-h-paratolyl-a-phenylformazyl*,

$$C_6H_4Me\cdot N_2H\dot{:}C(NPh)\cdot N_2Ph,$$

which is red with a bronze lustre, and melts at 173—174°. It will be noticed that this compound and the acid from which it is derived melt at nearly the same temperatures as their isomerides mentioned above.

Formazylbenzene, $N_2HPh\dot{:}CPh\cdot N_2Ph$, is obtained by the action of diazobenzene on the phenylhydrazone of either benzaldehyde or glyoxylic acid; it is red with a greenish metallic lustre, and melts at 173·5°. *Diparatolylformazylbenzene*, $C_6H_4Me\cdot N_2H\dot{:}CPh\cdot N_2\cdot C_6H_4Me$, from paradiazotoluene and the paratolylhydrazone of benzaldehyde, is almost black with a greenish lustre, and melts at 166°. Like it in appearance is *h-phenyl-a-paratolylformazylbenzene*,

$$N_2HPh\dot{:}CPh\cdot N_2\cdot C_6H_4Me,$$
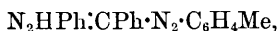
from paradiazotoluene and the phenylhydrazone of benzaldehyde; this melts at 155·5°, and also strongly resembles *h-paratolyl-a-phenylformazylbenzene*, $C_6H_4Me\cdot N_2H\dot{:}CPh\cdot N_2Ph$, melting at 155°, from diazobenzene and the paratolylhydrazone of benzaldehyde. When formazylbenzene is heated with sulphuric acid, in the presence of acetic acid, aniline and *phenophenyltriazine*, $C_6H_4{<}{\overset{\text{N:N}}{\underset{\text{N:CPh}}{\big|}}}$, are formed; the latter is yellow, and melts at 123°. Similarly *h-phenyl-a-para-tolylformazylbenzene* yields aniline and *methylphenophenyltriazine*, $C_6H_3Me{<}{\overset{\text{N:N}}{\underset{\text{N:CPh}}{\big|}}}$, which is yellow, and melts at 95—96°. Curiously enough, *h-paratolyl-a-phenylformazylbenzene* yields the same pro-ducts, and not, as would be expected, paratoluidine and phenophenyl-triazine. C. F. B.

Decomposition-products of Formazyl-compounds. By H. v. PECHMANN and P. RUNGE (*Ber.*, **27**, 1693—1699; compare the first paragraph of the preceding abstract).—A number of formazyl-com-pounds have been reduced with zinc-dust and sulphuric acid in the presence of alcohol. Two atoms of hydrogen are taken up, and the substance formed, reacting with a molecule of water, splits up into a mixture of hydrazine and hydrazide. But formazyl-compounds of

the type $N_2HX:CR\cdot N_2Y$ do not yield only the products which would be expected, as the result of the changes

$$N_2HX:CR\cdot N_2Y \rightarrow N_2HX:CR\cdot N_2H_2Y \rightarrow N_2H_3X + CRO:N_2H_2Y ;$$

they also yield the hydrazine, N_2H_3Y, and the hydrazide, $CRO:N_2H_2X$, which would be expected, as the products of the reduction of the isomeric formazyl-compound $N_2HY:CR\cdot N_2X$. This anomaly might be explained by supposing the substance $N_2HX:CR\cdot N_2H_2Y$ to form, with a molecule of water, a compound that afterwards decomposes in two different ways. This anomalous reaction is exhibited by *h*-phenyl-*a*-paratolylformazylbenzene. Formazyl hydride itself, of course, gives normal products, as here the groups X and Y are identical; both = Ph. Those compounds, in which the imido-nitrogen atom is replaced, can, of course, give only one hydrazine and one hydrazide on reduction. Thus acetylformazylhydride, $N_2AcPh:CH\,N_2Ph$, yields only *as-acetylphenylhydrazine*, N_2H_2AcPh, and *s*-formylphenylhydrazine, $CHO\cdot N_2H_2Ph$. And the two isomerides, *h-acetylphenyl-a-paratolyl-formazylhydride*, $N_2AcPh:CH\cdot N_2\cdot C_6H_4Me$ (orange-yellow prisms melting at 157·5°), and *h-acetylparatolyl-a-phenylformazylhydride*,

$$C_6H_4Me\cdot N_2Ac:CH\cdot N_2Ph$$

(yellow needles melting at 161°), a mixture of which is obtained by heating *either* of the two phenylparatolylformazylformic acids (see preceding abstract) with acetic anhydride, yield, the first *as*-acetylphenylhydrazine and *s*-formylparatolylhydrazine, the second *as*-acetylparatolylhydrazine and *s*-formylphenylhydrazine. And these two isomerides, further, on hydrolysis yield respectively *h-phenyl-a-paratolylformazylhydride*, $N_2HPh:CH\cdot N_2T$, and *h-paratolyl-a-phenylformazyl*, $N_2HT:CH\cdot N_2Ph$; these cannot be distinguished from each other, for both form ruby-red plates, both melt at 116—117°, and both, when treated with acetic anhydride, yield the same mixture of the two isomeric acetic derivatives mentioned above.   C. F. B.

Reduction of Paradinitrodiazoamidobenzene. By B. PAW-LEWSKI (*Ber.*. **27**, 1565—1568).—Paradinitrodiazoamidobenzene is best prepared by adding an excess of amylic nitrite to a solution of paranitraniline in ethylic acetate. The pure substance melts at 231° (stated as 223° by Meldola and Streatfield, Trans., 1886, 626). The reduction of this substance has been carried out by these two chemists, who observed the production of a magenta-red coloration, but only obtained paraphenylenediamine. The author has obtained three distinct products, the third of which will form the subject of a separate communication.

(1.) When the dinitro-compound is heated with weak alcoholic potash or alcoholic sodium ethoxide, a dark coloured powder is formed which may be purified by dissolving it in ethylic acetate and precipitating with alcohol. It then forms a brick-red powder of the composition $C_{12}H_{11}N_5O_2$, melts and decomposes at 225—227°, and is sparingly soluble; its solutions in methylic alcohol, ethylic acetate, and alcohol are yellow, and give a magenta-red coloration with potash, which disappears on acidification.

(2.) When this solution or paradinitrodiazoamidobenzene itself is boiled with concentrated alcoholic potash, an amorphous, reddish-brown precipitate is formed which has the composition $C_{12}H_9N_5O$, decomposes without melting at 255—260°, and gives red solutions in methylic alcohol, acetone, and ethylic acetate.

The author ascribes the following formulæ to these compounds on account of the method of formation and their relation to each other.

$$C_6H_4 < ^{N(OH)\cdot(OH)N}_{N\overline{===}N\overline{---}NH} > C_6H_4$$
Paradiazoamidodiazodihydroxybenzene.

$$C_6H_4 < ^{N\overset{O}{\overbrace{}}N}_{N:N\cdot NH} > C_6H_4$$
Paradiazoamidoazoxybenzene.
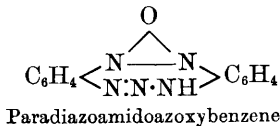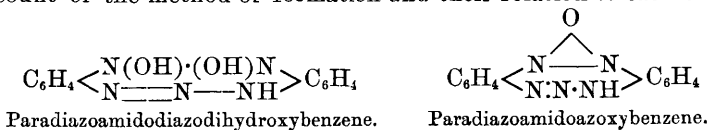
A. H.

Stereoisomeric Diazoamido-compounds. By A. HANTZSCH (*Ber.*, **27**, 1857—1866; compare this vol., i, 455).—The substances usually termed diazoamido-compounds may be more conveniently termed benzenediazoamides, anilides, &c., ordinary diazoamidobenzene being, for example, benzeneantidiazoanilide.

Benzenesyndiazoanilide, $^{Ph\cdot N}_{NHPh\cdot N}^{||}$, is formed when an alcoholic solution of pure diazobenzene chloride is treated in the cold with a solution of sodium methoxide in methylic alcohol, or when a concentrated aqueous solution of diazobenzene chloride, prepared from the pure crystalline chloride, is brought into a concentrated solution of sodium carbonate which contains some of the solid carbonate. It is also formed in the pure state when a mixture of diazobenzene chloride and aniline hydrochloride in exactly molecular proportion is dissolved in a little water and treated in the same manner. The requisite mixture is best obtained by the decomposition of ordinary diazoamidobenzene with hydrogen chloride, since, if the exact proportions be not employed, the product always contains more or less of the ordinary (anti)diazoamidobenzene. The nature of the action which occurs in this preparation has not yet been ascertained. Benzenesyndiazoanilide is a pale yellow, microcrystalline powder, which is insoluble in water, sparingly soluble in alcohol, readily in ether, very readily in benzene. The solutions readily undergo decomposition, nitrogen being evolved, and a resinous substance formed. When the pure substance is kept, it slowly becomes dark coloured, and changes into a viscid mass. It deflagrates brilliantly when heated to 75°, explodes feebly when brought into concentrated sulphuric acid, and sometimes explodes spontaneously when exposed to sunlight.

Paratoluenesyndiazotoluidide, $^{C_6H_4Me\cdot N}_{C_6H_4Me\cdot NH\cdot N}^{||}$, is best prepared from paradiazotoluene chloride and sodium carbonate or methoxide, the action of sodium carbonate on a molecular mixture of diazotoluene chloride and toluidine hydrochloride always giving rise to a mixture of the two isomerides. It closely resembles the benzene compound but is more stable, decomposing when heated at 78°, and not exploding in the sunlight.

Parabromobenzenesyndiazobromanilide, $\dfrac{C_6H_4Br\cdot N}{C_6H_4Br\cdot NH\cdot N}$, is formed as

a light yellow powder when an ordinary diazotised solution of para-bromaniline is brought into an excess of saturated aqueous sodium carbonate. It explodes readily when gently rubbed, and has not yet been closely examined.

All these syn-compounds are decomposed in ethereal solution by hydrogen chloride, a diazo-salt and the hydrochloride of the corresponding base being formed, so that they are structurally diazo-compounds, and do not possess a different structural form such as

$PhN{<}\begin{smallmatrix}NPh\\|\\NH\end{smallmatrix}$. They also, like all the derivatives of the syn-diazo-series,

have the power of combining directly with phenols to form colouring matters. This is best shown by covering the syn-diazoanilide with alcohol or acetone, and adding a solution of β-naphthol in soda containing as little free alkali as possible. A deep coloration is produced, whereas the ordinary anti-diazoanilides give no trace of a colouring matter when treated in this way. When benzenesyndiazoanilide is dissolved in alcoholic ammonia in the cold, and the solution evaporated after some time, benzeneantidiazoanilide is deposited along with a very small amount of resin. Alcoholic soda produces the same change, but rather more resin. The toluene compound undergoes the change even more readily than the benzene derivative. The behaviour of these compounds, then, confirms the general rule that the anti-compounds are stable in alkaline solutions. All the aromatic and mixed diazoamido-compounds previously prepared belong to the anti-series.

It is possible that in some cases the diazoamido-compounds are tautomeric; thus benzenediazotoluidide, $NPh\dot{:}N\cdot NH\cdot C_6H_4Me$, may react as though it had the tautomeric formula, $NHPh\cdot N\dot{:}N\cdot C_6H_4Me$, which is identical with the formula of toluenediazoanilide, and this may account for the fact that the diazoamido-compounds, prepared from diazobenzene and toluidine and from diazotoluene and aniline, are apparently identical. A. H.

Possible Stereoisomerism of Ethers of Metachloroquinone-oxime. By F. KEHRMANN (*Annalen*, **279**, 27—39).—As stated by Bridge (this vol., i, 25), two isomeric benzoyl derivatives are obtained from metachloroquinoneoxime; but the statement of this chemist that this is due to the non-homogeneity of the oxime is erroneous. As a matter of fact, the author shows that both these benzoyl derivatives, which melt at 192° and 162° respectively, are converted into meta-chloroquinoneoxime (m. p. 141°) when heated with dilute soda. Both benzoyl derivatives, when treated successively with alkali and nitric acid, are converted into orthochlororthoparadinitrophenol (m. p. 112—113°); and when treated first with alkali and subsequently with stannous chloride and hydrochloric acid, they each yield chloroparamidophenol (m. p. 151—152°). When either of the benzoyl derivatives is hydrolysed with alkali, and the product reconverted into the benzoyl derivative, this proves in each instance to be a mixture

consisting principally of the higher melting compound. The author regards it most probable that the two benzoyl derivatives are stereo-isomerides.

When chloroquinone is treated with α-methylhydroxylamine hydrochloride, and the product is crystallised from light petroleum, a chloroquinonemethoxime, crystallising in needles and melting at 122—123°, is obtained (compare Bridge, *loc. cit.*). A small quantity of an isomeride, crystallising in prisms and melting at 114—115°, was also isolated. The author has, however, not succeeded in obtaining the chloroquinonemethoxime (m. p. 97°) described by Bridge, but he finds that when the isomerides mentioned above are fused and allowed to resolidify, the melting point of both is 97°. The isomerides may be recrystallised unchanged from hot nitric acid of sp. gr. 1·4, but are readily converted into orthochloroparamidophenol on treatment with stannous chloride and hydrochloric acid, a fact which proves that they are structurally identical.

The author is engaged on further experiments; he states that he has succeeded in preparing metachloroquinoneoxime in a state of purity by means of the acetyl derivative, which latter also exists in two modifications. A. R. L.

Dinitrophenyl Ethers of Oximes. By A. WERNER (*Ber.*, **27**, 1654—1657).—The *dinitrophenyl ethers* of the following oximes were prepared; the method adopted was to mix the oxime (1 mol.) with sodium ethoxide (1 mol.), and then add 1 : 2 : 4-chlorodinitrobenzene, when the desired compound crystallised out. These ethers on hydrolysis generally yield dinitrophenol; they could not be made to yield the dinitrophenyl ether of hydroxylamine. The formulæ, melting points, and colour, if any, of the ethers prepared are given below against the names of the oximes from which they are respectively derived; R stands for the group $-C_6H_3(NO_2)_2$. *Antibenzaldoxime*, $CHPh\!:\!NOR$, 139—140°, yellow; *antimetanitrobenzaldoxime*, $NO_2\!\cdot\!C_6H_4\!\cdot\!CH\!:\!NOR$, 188°; *benzenylamidoxime*, $NH_2\!\cdot\!CPh\!:\!NOR$, 181°, yellow; *acetoxime*, $CMe_2\!:\!NOR$, 90°; *antiethylbenzhydroximic acid*, $OEt\!\cdot\!CPh\!:\!NOR$, 150—152°; *menthoneoxime*, $C_{10}H_{18}\!:\!NOR$; *lævo-rotatory*, 112°; *dextro-rotatory*, 72°. C. F. B.

The Iodonium Bases. By C. HARTMANN and V. MEYER (*Ber.*, **27**, 1592—1599; compare this vol., i, 242).—*Diphenyliodonium nitrate*, $IPh_2\!\cdot\!NO_3$, is obtained as a white crystalline precipitate, when a strong solution of the base is neutralised with concentrated nitric acid. It dissolves very readily in hot water and separates on cooling in small plates or compact spear-shaped crystals. It melts at 153—154°, forming a clear liquid which soon decomposes, whilst if a larger quantity of it is heated it explodes gently. This salt may also be obtained by dissolving the chloride in fuming nitric acid.

Diphenyliodonium hydrogen sulphate, $IPh_2\!\cdot\!HSO_4$, is so readily soluble that it cannot be recrystallised from water, but may be purified by precipitating its alcoholic solution with ether. It has

an acid reaction, melts at 153—154°, and decomposes at a somewhat higher temperature.

Diphenyliodonium acetate, $IPh_2 \cdot OAc$, is best prepared by shaking iodoxybenzene with aqueous soda, acidifying with acetic acid, filtering and cooling the filtrate. The acetate melts and decomposes at 120°, and cannot be recrystallised from water. It gives up the whole of its acetic acid when distilled in a current of steam.

Diphenyliodonium periodide, $IPh_2 \cdot I_3$. Like the alkylammonium iodides, phenyliodonium iodide forms a crystalline additive compound with iodine. It is prepared by grinding the iodide with alcoholic iodine, crystallises from alcohol in almost black needles, with a diamond lustre, and melts at 138°.

Diphenyliodonium mercurichloride, $IPh_2 \cdot HgCl_3$, crystallises from water in white, very refractive needles, and melts and decomposes at 172—175°.

The *aurochloride*, $IPh_2 \cdot AuCl_4$, which is almost insoluble in cold water, crystallises in golden-yellow needles and melts and decomposes at 134—135°. The *platinochloride*, $(IPh_2)_2PtCl_6$, is only sparingly soluble in hot water and crystallises in microscopic needles, melting and decomposing at 184—185°.

The analogy between the iodonium compounds and the salts of the heavy metals also extends to the sulphur compounds of the base. When yellow ammonium sulphide is added to a solution of the base, a thick, orange-red precipitate is produced, resembling antimony sulphide. This precipitate is stable at 0°, but at the ordinary temperature it undergoes rapid decomposition and yields a mobile oil which consists of moniodobenzene and a mixture of phenylic sulphides, mainly the trisulphide, Ph_2S_3. The orange-red compound is, therefore, probably *diphenyliodonium trisulphide*, $(IPh_2)_2S_3$. The corresponding *monosulphide*, $(IPh_2)_2S$, is obtained as a pale yellow precipitate when sodium monosulphide is added to a solution of the base. It behaves in a similar manner to the trisulphide, yielding moniodobenzene and phenylic sulphide, Ph_2S.

When an aqueous solution of the free base is treated in the cold with 5 per cent. sodium amalgam, reduction takes place quantitatively according to the equation

$$2IPh_2 \cdot OH + 4H = IPh_2I + 2C_6H_6 + 2H_2O.$$

When the iodide formed is boiled with aqueous soda it yields iodobenzene and phenol.

The preparation of the iodonium base by means of caustic soda gives a smaller yield (55—63 per cent.) than is obtained by the use of silver oxide (93 per cent.), but has the advantage that the iodic acid formed in the reaction dissolves in the liquid and on treatment with sulphurous acid yields exactly the amount of hydriodic acid required to react with the base, so that no potassium iodide need be added, and nearly all the iodine used is converted into the iodonium iodide. A small amount (3·5 per cent.) of the base is also formed in the preparation of iodoxybenzene from iodosobenzene by means of steam.

The physiological action of the chloride of the base resembles that

of ammonium salts, on the one hand, and of heavy metals such as lead and thallium on the other.

Doses of 0·02—0·03 gramme produce total paralysis in frogs, both the motor nerve endings and the muscle substance being affected. A dose of 0·08 per kilo. proves fatal to rabbits, the spinal chord and *medulla oblongata* being also affected. A. H.

The Law of Etherification of Aromatic acids. By V. MEYER and J. J. SUDBOROUGH (*Ber.*, **27**, 1580—1592).—Benzoic acid and its substitution products as a rule yield 90 per cent. of an ethereal salt when treated with methylic alcohol and hydrochloric acid in the cold. The symmetrical trisubstitution products of benzoic acid, however, are an exception to this rule and yield no ethereal salt whatever under the same conditions. In some cases a small amount of ethereal salt is obtained from such compounds (this vol., i, 243), but this is due to impurities, and when these have once been removed by etherification, the purified acid yields no ethereal salt at all. This rule holds absolutely for all the 1 : 3 : 5-trisubstitution derivatives of benzoic acid (Me,NO$_2$,Br, and COOH) with which experiments have been made, except those containing one or more hydroxyl-groups. The same is true of all substituted benzoic acids in which the hydrogen atoms 2 : 6 [COOH = 1] have been replaced by other atoms or groups. Thus *tetrabromobenzoic acid* [COOH : Br$_4$ = 1 : 2 : 3 : 4 : 6] gives no ethereal salt under the conditions described above. This acid is prepared by means of the diazo-reaction from tribromometamidobenzoic acid and forms colourless needles, melting at 173—174°, which are sparingly soluble in hot water.

Tribromometamidobenzoic acid

$$[COOH : Br_3 : NH_2 : = 1 : 2 : 4 : 6 : 3]$$
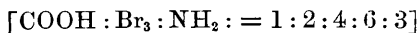
and *nitrotetrabromobenzoic acid* [COOH : Br$_4$: NO$_2$ = 1 : 2 : 3 : 4 : 6 : 5] also give no ethereal salts. The latter of these acids is obtained by the nitration of the tetrabromo-acid described above, and forms colourless needles, melting at 235°.

2 : 4-*Dibromobenzoic acid*, on the other hand, yields 95 per cent. of ethereal salt. This acid is obtained from 2 : 4-dibromaniline by means of Sandmeyer's reaction; it forms slender needles and melts at 163—164°. Finally, 2 : 6-*dibromobenzoic acid* yields no ethereal salt. This acid, which may be obtained from 2 : 6-dibromaniline in a similar manner to the foregoing, forms small needles melting at 136—137°.

The acids which do not yield ethereal salts when treated with alcohol and hydrochloric acid, can readily be converted into these substances by the action of methylic iodide on their silver salts.

The authors ascribe this remarkable behaviour to a stereochemical cause, the substituent groups being supposed by them to hinder the introduction of the alkyl group to such an extent that under the prescribed conditions the reaction does not proceed. Acids in which the carboxyl-group is connected with the benzene nucleus by means of an intermediary carbon atom readily undergo etherification. Thus mesitylacetic acid, C$_6$H$_2$Me$_3$·CH$_2$·COOH, yields 96 per cent. of

the *methylic* salt, which boils at 255—256°; and mesitylglyoxylic
acid, $C_6H_2Me_3 \cdot CO \cdot COOH$, behaves in a similar manner, the *methylic*
salt boiling at 273—275°. This behaviour is quite in accordance
with the stereochemical view of the phenomenon.

Among the derivatives of mellitic acid, the behaviour of pyromel-
litic acid $[(COOH)_4 = 1:2:4:5]$, prehnitic acid $[(COOH)_4 =
1:2:3:4]$ and mellitic acid (benzenehexacarboxylic acid) has been
examined and found in exact accordance with the rule established
above. Thus mellitic acid does not undergo etherification, prehnitic
acid only yields a *dimethylic salt* (melting at 176—177°) and pyro-
mellitic acid gives the tetramethylic salt. The constitution of a sub-
stituted benzoic acid may, therefore, be readily tested in this way
and the method may also be used for purifying or isolating those acids
which will not undergo etherification.   A. H.

Isomeric Nitrobenzoic acids. By OECHSNER DE CONINCK *(Compt.
rend.*, **118**, 1104—1105 and 1207—1208).—The mean solubilities of
the three nitrobenzoic acids in water are as follows: ortho-acid at
11·2°, $\alpha = 0·0533$, meta-acid at 11·9°, $\alpha = 0·0268$, par-acid at 12·2°,
$\alpha = 0·0024$.

Orthonitrobenzoic acid is rapidly carbonised when gently heated
with ordinary sulphuric acid, but the meta- and para-acids simply
dissolve and at most become amber coloured. When heated with
ordinary nitric acid, orthonitrobenzoic acid yields a colourless
solution, the meta-acid a slightly yellow solution, and the para-
acid dissolves only partially and yields a pale yellow solution. With
fuming nitric acid the results are similar, but all three acids dissolve
completely.

Warm aqua regia completely dissolves the ortho-acid and partially
dissolves the meta- and para-acids, bright yellow solutions being
formed.

The action of nitric acid and of aqua regia affords a ready means of
distinguishing nitrobenzoic acids from amidobenzoic acids. A dilute
aqueous solution of chromic acid likewise distinguishes the amido
from the nitro-derivatives since it has no action on the latter below
its boiling point.

All three nitrobenzoic acids are unaffected when exposed to sun-
light in contact with dilute hydrochloric acid. When exposed in
contact with dilute nitric acid, the meta-derivative slowly acquires a
pale yellow coloration. When moderately concentrated solutions in
acetone are exposed to sunlight, there is no change, but with dilute
alcoholic solutions, the para-acid becomes bright yellow and the
meta-acid pale yellow.

In all cases where there is any reaction at all, two of the nitro-
benzoic acids behave similarly, whilst the third behaves differently
from the other two.   C. H. B.

Formation of Ethereal Salts of Aromatic acids. By B. LEPSIUS
(Ber., **27**, 1635).—Symmetrical trinitrobenzoic acid exemplifies V.
Meyer's rule (this vol., i, 243); only 1·66 per cent. of methylic salt
is formed.   C. F. B.

Preparation of Iodoxybenzoic acid. By C. HARTMANN and V. MEYER (*Ber.*, **27**, 1600).—A more convenient method for the preparation of iodoxybenzoic acid than that originally described (Abstr., 1893, i. 577) is to dissolve 5·3 grams of iodosobenzoic acid in 4 grams of aqueous soda and saturate the cold solution with chlorine. After acidifying, the residue is extracted with ether to remove orthoiodobenzoic acid, and the iodoxybenzoic acid is separated from unaltered iodosobenzoic acid as previously described. Iodoxybenzoic acid partially decomposes when kept, a large amount of it being converted into iodosobenzoic acid. A. H.

Sodium Borosalicylate. By P. ADAM (*Bull. Soc. Chim.*, [3], **11**, 204—206).—It is well known that the solubility of salicylic acid in water is greatly increased by the addition of borax On evaporating an aqueous solution containing sodium salicylate and boric acid in molecular proportion, a syrupy liquid is obtained, which slowly deposits *sodium borosalicylate*, $C_7H_4O_4BNa$, as a white, amorphous powder. It is soluble in 4 parts of cold water, and in methylic, ethylic, and amylic alcohols, ethylic acetate, &c. Solutions of the salt do not give the reactions of boric acid; its alcoholic solution does not burn with the green flame characteristic of this acid. Borosalicylic acid does not seem to exist in the free state; on acidifying the solution of the sodium salt, boric and salicylic acids are deposited. W. J. P.

Action of Phenylhydrazine on Ethylic Benzalmalonate. By W. WISLICENUS (*Annalen*, **279**, 23—26).—Wislicenus and Reitzenstein (this vol., i, 133) have shown that benzylidenediketohydrindene is decomposed by phenylhydrazine. The author now finds that when ethylic benzalmalonate, $CHPh(COOEt)_2$, is warmed with alcohol and phenylhydrazine for an hour, benzylidenephenylhydrazone and ethylic malonate are formed. The ethylic salt,

$$C(COOEt)_2{:}C(COOEt)_2,$$
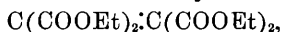
does not decompose in this manner when treated with phenylhydrazine. A. R. L.

Formation of Ethereal Salts of Chlorhydrin and of Dichlorhydrin. By C. GÖTTIG (*Ber.*, **27**, 1602—1604).—The author has investigated the action of hydrogen chloride on a mixture of glycerol and various acids. Phthalic acid yields a product free from chlorine; gallic acid and succinic acid resemble the hydroxybenzoic acids (Abstr., 1892, 715), and give ethereal salts of dichlorhydrin, which have not been isolated. Paramethoxybenzoic acid yields an ethereal salt of dichlorhydrin; it crystallises in needles, melts at 74—76°, and is somewhat difficult to hydrolyse. As the compound is formed above 100°, it is probably a derivative of α-dichlorhydrin, and has the formula $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}OCH_2{\cdot}CHCl{\cdot}CH_2Cl$. J. B. T.

Acids from Benzoylacetonedicyanhydrin. By M. CARLSON (*Ber.*, **27**, 1571—1574; compare Abstr., 1892, 1471).—The author has succeeded in obtaining larger amounts of the products of this reaction.

When crude benzoylacetonedicyanhydrin is dissolved in hydrochloric acid, and the liquid then saturated with hydrogen chloride, hydrocyanic acid is liberated, and an acid of the formula $C_{11}H_{12}O_3$ produced, along with acetophenone, and a large amount of resin. This acid forms colourless granules, and melts at 124—125°. It is monobasic, and yields an unstable, amorphous, *silver* salt, $C_{11}H_{11}AgO_3$. It is an unsaturated acid, and combines with 1 mol. of bromine, forming a *bromide*, $C_{11}H_{12}Br_2O_3$, which crystallises from light petroleum in colourless prisms, softens at 155°, and melts at 163°.

When the hydrolysis of crude benzoylacetonedicyanhydrin is carried out by means of boiling alcoholic potash, on the other hand, an isomeric acid, $C_{11}H_{12}O_3$, is produced. This crystallises in long needles, melts at 101—102°, and, like its isomeride, is very sparingly soluble in cold water. It is also a monobasic acid, and combines with 1 mol. of bromine to form a crystalline bromide. The constitution of these acids is being made the subject of further investigation.

A. H.

Aniline and Ethylic Isodibromosuccinate. By D. VORLÄNDER (*Ber.*, **27**, 1604—1605).—Ethylic dianilidosuccinate,

$$COOH\cdot CH(NHPh)\cdot CH(NHPh)\cdot COOH,$$
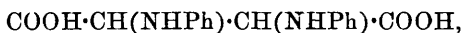
is formed by the action of aniline on ethylic isodibromosuccinate in alcoholic solution. Attempts to convert the free acid into indigo by the action of dehydrating agents, such as fuming sulphuric acid, or phosphoric anhydride, were unsuccessful, but three times out of 40—50 experiments, indigo was produced by fusing the acid with potash, the necessary conditions for its formation, however, could not be determined.

J. B. T.

Application of Friedel and Crafts' Reaction to Thiophenol Ether. By K. AUWERS and C. BEGER (*Ber.*, **27**, 1733—1741).— *Thioethylbenzophenone*, $SEt\cdot C_6H_4\cdot COPh$, is formed when thiophenyl ethyl ether is warmed in solution in carbon bisulphide with benzoic chloride and aluminium chloride. It forms lustrous, white prisms, which are sparingly soluble in light petroleum, and melt at 82—83°. When this ketone is treated with alkaline hydroxylamine solution, it yields a mixture of two stereochemically isomeric oximes, which may be separated by V. Meyer's method (*Annalen*, **264**, 116).

Antithioethylbenzophenoneoxime crystallises from ethylic acetate in short compact, vitreous prisms, melting at 133—134°, and readily soluble in the usual solvents, with the exception of light petroleum. The *hydrochloride* is crystalline, and yields the original substance when decomposed with soda. The *acetate* forms compact, lustrous prisms melting at 99—100°. When the oxime is heated with alcohol, or an alcoholic solution of an alkali, it is partially converted into the isomeride of lower melting point. The constitution of the oxime is shown by the fact that when it is dissolved in ether and treated with phosphorus pentachloride, it is converted into *thioethylbenzanilide*, $SEt\cdot C_6H_4\cdot C(OH){:}NPh$, which crystallises from alcohol in

snow-white plates with a satiny lustre, melting at 158°. This substance, when heated with hydrochloric acid, yields thioethylbenzoic acid, $SEt \cdot C_6H_4 \cdot COOH$, and aniline.

Synthioethylbenzophenoneoxime crystallises in slender needles, is slightly more soluble than the anti-compound, and, when heated, softens at 94°, and melts at 96°. Like its isomeride, it yields a crystalline hydrochloride, and is partially converted into the higher melting form by alcohol at 100°. The *acetate* forms slender needles melting at 58—60°. When treated with phosphorus pentachloride, this isomeride is converted into the *thioethylanilide of benzoic acid*, $C_6H_5 \cdot CO \cdot N \cdot C_6H_4 \cdot SEt$, which melts at 145°, and when treated with hydrochloric acid yields benzoic acid and thioethylaniline,

$$SEt \cdot C_6H_4 \cdot NH_2;$$

the latter may be recognised by means of its *acetyl* derivative, $SEt \cdot C_6H_4 \cdot NHAc$, which forms lustrous needles melting at 108—110°.

Thioethylacetophenone, $SEt \cdot C_6H_4 \cdot COMe$, is obtained in a similar manner to the benzoyl derivative, and forms lustrous plates, which melt at 43·5°, and are slightly soluble in light petroleum. This ketone only yields one *oxime*, which crystallises in long, thin needles melting at 91°.

Thiophenyl ethyl ether also reacts with chloroformamide in the presence of aluminium chloride to form *thioethylbenzamide*,
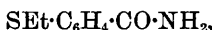
$$SEt \cdot C_6H_4 \cdot CO \cdot NH_2,$$

which crystallises in broad, lustrous needles melting at 169—170°, *Thioethylbenzoic acid*, $SEt \cdot C_6H_4 \cdot COOH$, also forms broad, flat needles, and melts at 146°.

When phenylthiocarbimide is employed in this reaction, the *thioanilide of thioethylbenzoic acid*, $SEt \cdot C_6H_4 \cdot CS \cdot NHPh$, is obtained; this forms golden-yellow, lustrous plates melting at 140—141°. When it is oxidised with potassium ferricyanide, it is converted into *thioethylbenzenylamidophenyl mercaptan*, $SEt \cdot C_6H_4 \cdot C {\displaystyle \ll_N^S} > C_6H_4$, which forms white needles melting at 101—102°. A. H.

Constitution of the Rosanilines. By A. ROSENSTIEHL (*Bull. Soc. Chim.*, [3], **11**, 212—213; compare Abstr., 1893, i, 332).—A claim to priority as against Stock (Abstr., 1893, i, 472). W. J. P.

The Coloured and Colourless Derivatives of Di- and Triphenylmethane. By A. ROSENSTIEHL (*Bull. Soc. Chim.*, [3], **11**, 213—216).—The author considers that V. Richter's and Noelting's rules respecting the colour of phenylmethane derivatives must be combined, in order to represent the facts. W. J. P.

Condensation of Aldehydes with α-Naphthaquinol and α-Naphthaquinone. By J. WURGAFT (*J. pr. Chem.*, [2], **49**, 551—552).—By saturating a cold mixture of α-naphthaquinol (2 mols.) and benzaldehyde (1 mol.) with hydrogen chloride, red, rhombic

crystals of the compound $C_{27}H_{19}ClO_4 + H_2O$ are obtained. The crystals dissolve in alkalis yielding a blue solution, which slowly becomes brown. Since the same compound is obtained by the direct action of benzotrichloride on α-naphthaquinol in glacial acetic acid, it is inferred that this chlorine derivative is *tetrahydroxydinaphthylcarbinol chloride;* the dechlorinated carbinol, $OH \cdot CPh[C_{10}H_5(OH)_2]_2$, and its *acetyl*-derivative, which crystallises in white, rhombic tables, and melts at 246°, were prepared. A similar red colouring matter is obtained by a like treatment of a mixture of α-naphthaquinone with benzaldehyde.   A. G. B.

Butylnaphthalene. By A. BAUR (*Ber.*, **27**, 1623).—Butyl-naphthalene (b. p. 280°) is prepared from naphthalene, isobutylic bromide, and aluminium chloride, and is sparingly volatile with steam. The *trinitro-derivative* forms granular crystals, melts at 79—80°, with previous softening at about 50°, and has no odour of musk.   J. B. T.

Ketones from Pinene Derivatives. By L. C. URBAN and E. KREMERS (*Amer. Chem. J.*, **16**, 404—406).—Nitrosopinene, whilst stable towards sulphuric acid, yields with hydrochloric acid a *ketone*, $C_{10}H_{14}O$, having a peppermint odour, and, therefore, probably a β-ketone.   L. T. T.

The Menthol Group. By L. C. URBAN and E. KREMERS (*Amer. Chem. J.*, **16**, 395—404).—The rotation of menthene (Abstr., 1892, 1479) is now given as $[\alpha]_D = +31 \cdot 83°$ (instead of $+26 \cdot 40°$), and of the nitrosochloride, melting at 113°, as $[\alpha]_D = +13 \cdot 76°$. An inactive nitrosochloride melting at 128° has also been obtained. *Menthene nitrosate*, $C_{10}H_{18}N_2O_4$, melts at 98°, and is optically inactive. *Menthene nitrosobenzylamine*, $NO \cdot C_{10}H_{18} \cdot NH \cdot C_7H_7$, from the nitrosate or nitroso-chloride, melts at 107°, and is optically inactive. No piperidine base could be obtained, the alkaloïd acting on the nitrosochloride like an alkali, and causing the separation of hydrogen chloride. *Nitroso-menthene*, produced by the action of alcoholic potash on the nitroso-chloride or nitrate, yields, on sublimation, colourless needles, is volatile in steam, melts at 67°, and is optically inactive. On reduc-tion, it yields an *amido*-compound, which, with the diazo-reaction, gives an unsaturated *secondary alcohol*, $C_{10}H_{18}O$, boiling at 210—215°. The amido-compound, which is, therefore, probably $C_{10}H_{17} \cdot NH_2$, rather than the saturated amine, $C_{10}H_{19} \cdot NH_2$, as anticipated, is being further investigated. In preparing the amine, small quantities of an *inactive menthene*, boiling at 204—206°, and volatile in steam, were produced. This yields an *oxime*, crystallising in needles, melting at 82°, and giving a crystalline hydrochloride. The menthene, on reduction by Beckmann's method, appears to give menthol, but the latter could not be fully identified. Nitrosomenthene is comparatively stable to-wards sulphuric acid, but with hydrochloric acid it yields an inactive *ketone*, $C_{10}H_{16}O$, a colourless oil of peppermint odour, boiling at 210—212°, and having a sp. gr. $= 0 \cdot 9150$ at 20°. When the ketone is treated with hydroxylamine, nitrosomenthene is re-formed, a proof

that the latter is a true oxime. The authors also discuss the bearings of recent work on the constitution of the menthol group.

<div align="right">L. T. T.</div>

Oxidation of Cyclic Compounds. By G. WAGNER (*Ber.*, **27**, 1636—1654).—Menthene, $\begin{matrix} CHMe\cdot CH_2\cdot CH \\ | \qquad\qquad || \\ CH_2 — CH_2\cdot C\cdot CHMe_2 \end{matrix}$ (1 mol.), was oxidised at about $0°$ with a 1 per cent. solution of potassium permanganate (containing 1 atom of oxygen); the products were a glycol, $\begin{matrix} CHMe\cdot CH_2\cdot CH(OH) \\ | \qquad\qquad\qquad | \\ CH_2 — CH_2\cdot C(OH)\cdot CHMe_2 \end{matrix}$; the corresponding keto-alcohol; a keto-acid (δ-isobutyryl-β-methyl-valeric),

$$COOH\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CO\cdot CHMe_2;$$
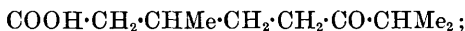
methyladipic acid, $COOH\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot COOH$, and acetic acid. The *keto-alcohol* boils at $104\cdot5$—$105\cdot5°$ under $13\cdot5$ mm. pressure, and has a sp. gr. $= 0\cdot9881$ at $0°/0°$; with phenylcarbimide it yields a *carbamate*, $NHPh\cdot CO\cdot O\cdot C_{10}H_{17}O_2$, melting at 155—$157°$, and with hydroxylamine an *oxime*, melting at 132—$133°$. The *glycol* is a viscid liquid, boiling at $129\cdot5$—$131\cdot5°$ under 13 mm. pressure; after a time it partially solidifies to crystals melting at $76\cdot5$—$77°$. Acetic anhydride at $150°$ converts it into a *diacetate*, boiling at 165—$172°$ (mixed, perhaps, with some monacetate, or with the acetate of an unsaturated alcohol), but also dehydrates a portion, forming a *terpene* which boils at 179—$180°$, and is probably identical with the product obtained by Berkenheim (Abstr., 1892, 867) from menthene dibromide and potash. The methyladipic acid melts at 93—$94\cdot5°$; immediately after solidifying, at $84\cdot5°$; after a short interval, again at 93—$94\cdot5°$. The *keto-acid* is a liquid boiling at 288—$290°$ (under 19 mm. pressure, at 182—$185°$). (In an attempt to prepare menthene by the action of strong sulphuric acid on menthol, it was found that menthane, that is hexahydrocymene, is the chief product.)

Pinol is oxidised by potassium permanganate, as above, to the glycol, $C_{10}H_{16}O(OH)_2$; this crystallises from ether and ethylic acetate in rhombic pyramids melting at 126—$127°$, from water in monoclinic tables melting at 128—$129°$, and with acetic anhydride yields a diacetate, which boils at 166—$167°$ under 17 mm. pressure, and does not solidify. (Wallach obtained rather different data; possibly he was working with a stereoisomeric pinol.) If permanganate was used in quantity equivalent to 3 atoms of oxygen per mol. of pinol, there were formed, in addition to pinol glycol, terpenylic acid, and a trace of terebic acid. Terpenylic acid is thus the main product of the further oxidation of pinol, and from the known formula of this acid (Schryver, Trans., 1893, 1338), the formula given below for pinol is deduced. Now pinol is formed by the action of dilute sulphuric acid on a compound which Sobrero obtained by the action of oxygen on turpentine in the presence of light; this compound is further identical with Wallach's pinol hydrate, obtained by adding hydrogen bromide to pinol, and then displacing the bromine by hydroxyl. Since this compound is formed from pinol, the formula below

is assigned to it, in preference to Wallach's formula, and it is supposed that, when hydrogen bromide is added to pinol, the double bond of the latter is not attacked, but the bond O—CH is destroyed. Pinol would thus be a dihydric alcohol, or glycol, and would still contain a double bond; this is in harmony with the fact that, when oxidised with permanganate, it does actually act like such a compound, yielding a *tetrahydric alcohol*, $C_{10}H_{20}O_4$, melting at 155·5—156°. The author also assigns new formulæ to several members of the terpene group; the most important of these are reproduced below, but the reasons which lead to their adoption it is impossible to give in an abstract.

$$\begin{array}{ll} CH_2\text{---}CH\cdot CMe_2 \\ \;| \qquad\quad | \\ COOH \quad CH_2\,| \\ \qquad\qquad CO\text{-}O \end{array}$$
Terpenylic acid.

$$\begin{array}{ll} CH_2\cdot CH\cdot CMe_2 \\ \;| \qquad | \\ CH \quad CH_2\,| \\ \;|| \qquad | \\ CMe\cdot CH\cdot O \end{array}$$
Pinol.

$$\begin{array}{ll} CH_2\cdot CH\cdot CMe_2\cdot OH \\ \;| \qquad | \\ CH \quad CH_2 \\ \;|| \qquad | \\ CMe\cdot CH\cdot OH \end{array}$$
Pinol hydrate.

$$\begin{array}{ll} CH_2\cdot CH \\ \;| \qquad | \quad\Big\backslash \\ CH \quad CH_2\;\Big\rangle CMe_2 \\ \;|| \qquad | \quad\Big/ \\ CMe\cdot CH \end{array}$$
Pinene.

$$\begin{array}{ll} CH_2\cdot CH\cdot CMe_2\cdot OH \\ \;| \qquad | \\ CH \quad CH_2 \\ \;|| \qquad | \\ CMe\cdot CH_2 \end{array}$$
Terpineole.
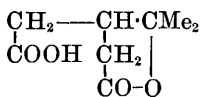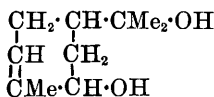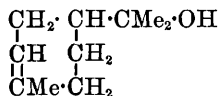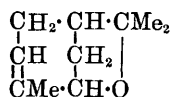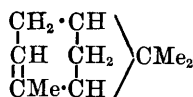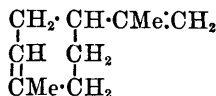
$$\begin{array}{ll} CH_2\cdot CH\cdot CMe{:}CH_2 \\ \;| \qquad | \\ CH \quad CH_2 \\ \;|| \qquad | \\ CMe\cdot CH_2 \end{array}$$
Limonene

C. F. B.

Oxidation of Menthone. By O. MANASSE and H. RUPE (*Ber.*, **27,** 1818—1822; compare Semmler, Abstr., 1893, i, 396).—β-methyl-adipic acid is produced almost quantitatively by the oxidation of menthone with dilute potassium permanganate solution at ordinary temperatures; it can be purified by precipitation from benzene by means of light petroleum, and melts at 88·5—89°. The electrolytic conductivity, $k = 0\cdot00397$; that of the synthetical acid, $k = 0\cdot00401$ $\mu\infty = 351$. The acid is dextrogyrate, $[\alpha]_D = +8\cdot42$. The *copper salt*, when precipitated at the ordinary temperature, is pale green and amorphous, but when heated with water, it forms slender, bluish-green, concentric prisms. The *iron salt* is yellowish-red; no sparingly soluble salts of the alkaline earths, zinc, or lead were obtained. The *anhydride* is formed by the action of acetic chloride on the acid, but not by heating the acid above its melting point; it is a colourless oil from which the acid is regenerated by exposure to the air. This is the first anhydride of the adipic series of acids which has been prepared, and its formation shows the influence of alkyl radicles in causing the convergence of the carboxyl groups in dicarboxylic acids. The oxidation of menthone proceeds in a similar manner to that of menthol, the intermediate keto-acid,

$$COPr^\beta\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot COOH,$$

being quickly, and almost completely, converted into β-methyladipic acid.   J. B. T.

Maclurin and Phloretin. By G. CIAMICIAN and P. SILBER (*Ber.*, **27**, 1627—1633).—Maclurin, $C_{13}H_{10}O_6$ (which is shown to crystallise with H_2O), when boiled with acetic anhydride and anhydrous sodium acetate, yields a compound, $C_{23}H_{18}O_{10}$, melting at 181—182°, and having the composition of a pentacetyl derivative, less 1 mol. of water. Now, if, as is sometimes supposed, maclurin is a phloroglucol salt of protocatechuic acid, it could only yield a *tetr*acetyl derivative. Its actual behaviour, however, resembles that of cotoïn (this vol., i, 256), and it is probably similarly constituted (being thus a ketonic compound), in spite of the fact that it does not react with phenylhydrazine or hydroxylamine. The compound, $C_{23}H_{18}O_{10}$, is hydrolysed by boiling with hydriodic acid, but the yellow product (? $C_{15}H_{10}O_6$), melting above 270°, was not obtained pure.

Phloretin, $C_{15}H_{14}O_5$, behaves in a similar manner, yielding a substance, $C_{23}H_{20}O_8$, which has the composition of a tetracetyl derivative, less 1 mol. of water. This substance melts at 173°, and yields, on hydrolysis, a yellowish compound, $C_{17}H_{14}O_5$, melting at 213°. These reactions again are probably analogous to those of cotoïn.

C. F. B.

Jalapin. By T. POLECK (*Arch. Pharm.*, **232**, 315—320).—The author replies to the strictures of Spirgatis (*Arch. Pharm.*, **232**, 241) on his previous work on jalapin (Abstr., 1893, i, 225).

W. J. P.

Reduction of α-Ethyl Pyridyl Ketone; Non-identity of α-Ethylpiperylalkine with Active Pseudoconhydrine. By C. ENGLER and F. W. BAUER (*Ber.*, **27**, 1775—1779; Abstr., 1891, 1504).—The authors have further studied the coniine and intermediate compounds obtained by the reduction of α-Ethyl pyridyl ketone as already described.

Coniine boils at 166—168·5°. The *hydrochloride* crystallises in silvery needles, and melts at 208—210°., The *platinochloride* is obtained as an oil which soon crystallises in orange-red nodules. The *double salt* with cadmium iodide has the same properties as the salt obtained from natural coniine. Optically active coniine can be prepared from the inactive synthetical substance by Ladenburg's method, that is, by crystallisation of the tartrate.

The high-melting modification of α-ethylpiperylalkine (m. p. 99—100°) is not identical with pseudoconhydrine (m. p. 101—102°), as is proved by a comparison of their salts as given below. The hydrobromides and hydrochlorides of both bases are very similar, and crystallise in white, hygroscopic needles. The salts of pseudoconhydrine are, however, more stable on exposure to air. The platinochlorides are very similar, and do not crystallise. *Ethylpiperylalkine cadmium iodide* crystallises in lustrous crystals, and melts at 121—122°. *Pseudoconhydrine cadmium iodide* is an oil which cannot be obtained crystalline. The flocculent precipitates which phosphomolybdic acid and mercuric chloride give with both bases are very similar. The difference of the two bases is clearly shown in the properties of the aurochlorides.

α-Ethylpiperylalkine aurochloride crystallises in beautiful yellow prisms, and melts at 138—139°. The crystals belong to the monoclinic system $(110):(1\bar{1}0) = 105°\ 27'$; $(110):(001) = 87°\ 30'$.

The aurochloride from pseudoconhydrine separates in beautiful yellow, rhombic crystals, and is identical with conhydrine aurochloride. The measurement of the crystals gave

$$a:b:c = 0.68059:1:0.73101;\ (110):(1\bar{1}0) =$$
$$68°\ 28'\ 42'',\ (011):(0\bar{1}1) = 72°\ 20'.$$

Thus, in the preparation of the aurochloride, pseudoconhydrine is converted into conhydrine.

The low-melting modification of α-ethylpiperylalkine has now been obtained in long, sharp-pointed needles melting at 69·5—71·5°. It is optically inactive. The *hydrochloride, hydrobromide,* and *platinochloride* are indistinguishable from the salts of the modification of high-melting point. The *aurochloride* crystallises in prisms, and melts at 135—136°. The *double salt* with *cadmium iodide* is a brownish-yellow oil which only crystallises with great difficulty.

E. C. R.

Ethereal Salts and Amides of Pyridinecarboxylic acids. By C. ENGLER and others (*Ber.,* **27**, 1784—1789; compare H. Meyer, this vol., i, 425).—Methylic picolinate, obtained in the usual way, boils at 232° (uncorr.), and melts at 14°. The *platinochloride* crystallises in orange-yellow prisms with $2H_2O$.

Ethylic picolinate is a colourless liquid, and boils at 243° (uncorr.) *Propylic picolinate* is a pale yellow oil, and boils at 258°; the *platinochloride* crystallises in orange-yellow plates. *Isobutylic picolinate* is a colourless oil, and boils at 261·5°. *Amylic picolinate* is a yellowish oil, boils at 278—279° with slight decomposition, and has an unpleasant odour; the *platinochloride* crystallises in beautiful yellow needles.

Picolinamide, $C_5NH_4\cdot CONH_2$, is most easily obtained by treating the ethylic salt with concentrated aqueous ammonia. It forms beautiful crystals, and melts at 107°. The *hydrochloride* crystallises in lustrous leaflets, which effloresce on exposure to air.

Picolinanilide, $C_5NH_4CONHPh$, melts at 76°. The *orthotoluidide* crystallises in silky needles, and melts at 64·5°; the *paratoluidide* in tablets melting at 104°; whilst the *naphthalide* crystallises in reddish needles, and melts at 128°.

The following compounds of nicotinic acid are described. The *methylic salt* boils at 204°, and melts at 38°. The *ethylic salt* boils at 218°. The *propylic salt* is a colourless oil, and boils at 232°. The *amylic salt* is a yellow oil, and boils at 259°. The *amide* crystallises in slender interlacing needles, and melts at 125°.

Quinolinic acid.—The *dimethylic salt* crystallises in beautiful lustrous leaflets, and melts at 53—54°. The *diethylic salt* is a yellowish oil, and boils and slightly decomposes at 280—285°. The *dipropylic salt* is a bright yellow oil, boils above 300°, has a penetrating odour, and darkens on exposure to air. The *diamide* melts at 209°.

Quinolinicimide, $C_5NH_3(CO)_2NH$, is obtained by heating the diamide at 200—209° as long as ammonia is evolved. It forms

colourless crystals, and melts at 227°. The *acetyl-compound* crystallises in slender, white needles, and melts at 161—162°. The *potassium salt* is obtained by allowing the imide and potassium hydroxide dissolved in alcohol to remain some time. It crystallises in aggregates of white needles, which contain $1H_2O$ after drying at 100°, and is very hygroscopic.

Phenyl quinolinicimide, $C_5NH_3(CO)_2NPh$, is obtained by heating the imide with aniline in a reflux apparatus. It crystallises in lustrous, interlacing needles, and melts at 228°. The *platinochloride* crystallises in red needles. E. C. R.

Preparation of Quinoline. By J. WALTER (*J. pr. Chem.*, [2], **49**, 549—550).—For the performance of Skraup's method of preparing quinoline a flask of large capacity is necessary in order to provide for the froth generated during the reaction. This inconvenience can be avoided by heating the nitrobenzene in a flask provided with a reflux condenser and a dropping funnel, from which the mixture of aniline, glycerol, and sulphuric acid may be added by degrees. In such an arrangement a flask of 800 c.c. capacity will suffice for a charge of 48 grams of nitrobenzene, whereas, by the old method, a 2000 c.c flask was necessary for 24 grams of nitrobenzene. The addition of the other constituents to 48 grams of nitrobenzene should be spread over three-quarters of an hour, and to keep their viscosity low the dropping funnel should be surrounded by a leaden steam coil. The distillation of the quinoline in steam may be effected in an iron vessel. A. G. B.

3 : 4 : 4′-Tribromoquinoline and 2 : 3 : 4 : 4′-Tetrabromoquinoline. By A. CLAUS and K. REINHARD (*J. pr. Chem.*, [2], **49**, 525—539; compare Abstr., 1888, 163; 1893, i, 667; this vol., i, 52, 53, 54, 382).—*3-Bromoquinoline methiodide* crystallises in yellow needles, and melts and partially decomposes at 278°. The *methochloride* forms colourless tables, begins to decompose at 224°, and melts at 238°; its *platinochloride* is described. The *ethiodide* melts and decomposes at 194°. The *ethochloride* melts at 145°.

By nitration in sulphuric acid, 3-bromoquinoline yields 4 : 3-nitrobromoquinoline (Abstr., 1890, 267), the *methochloride* of which crystallises in vitreous, topaz-coloured, rhombic prisms, and melts at 203°. The *platinochloride* of the methochloride is described. 4 : 3-Dibromoquinoline melts at 135°.

1 : 3-*Nitrobromoquinoline* is formed when 3-bromoquinoline is digested with nitric acid (sp. gr. 1·52) for several days. It crystallises in small, colourless, vitreous needles, melts at 170°, and is less soluble in hot alcohol than is the 4 : 3-derivative. The *platinochloride* is anhydrous, and melts at 265—268°. 1 : 3-*Amidobromoquinoline* crystallises in lustrous needles, which are generally tinted, melts at 76—77°, and is slightly soluble in hot water; the *hydrochloride* forms yellow-red needles with $2H_2O$, and melts at 236—237°; the *platinochloride* is described.

Both 3 : 1- (*loc. cit.*) and 3 : 4-bromoquinolinesulphonic acids are obtained by sulphonating 3-bromoquinoline with anhydro-sulphuric

acid, the proportion between them depending on temperature and concentration; the acids may be separated by means of their potassium salts, that of the 3 : 1-acid being the less soluble. The *potassium, calcium* ($1H_2O$), and *barium* salts of 3 : 1-bromoquinoline-sulphonic acid are described.

3 : 4-*Bromoquinolinesulphonic acid* crystallises with $1H_2O$ in tables, dissolves freely in hot water, and does not melt at 330°. The potassium ($1\frac{1}{2}H_2O$), *calcium* ($5H_2O$), *ammonium*, and *barium* salts are described.

The product of the bromination of 3 : 1-bromoquinolinesulphonic acid, described by Claus and Zuschlag (*loc. cit.*) as a tribromoquinoline melting at 185°, is a mixture of 1 : 3 : 4'-tribromoquinoline (m. p. 169°) and 1 : 3 : 4 : 4'-tetrabromoquinoline (m. p. 205°) (compare Abstr., 1891, 82). The bromination of 3 : 4-bromoquinoline-sulphonic acid yields 3 : 4 : 4'-tribromoquinoline (m. p. 149°) and 1 : 3 : 4 : 4'-tetrabromoquinoline. A. G. B.

Constitution of Cycloïd Systems. By W. MARCKWALD (*Annalen,* **279**, 1—23).—The author replies to Claus (this vol., i, 174). He considers that the results of his previous investigation (Abstr., 1893, i, 603) may be thus summarised:—The existence of para-bonds in benzene has never been recognised in a single instance, but, on the contrary, benzene-derivatives exhibit a resistance to the formation of para-bonds. Kekulé's benzene formula, granting that in poly-cycloïd systems oscillation is suppressed, does not stand in conflict with any known facts.

The fresh evidence brought forward by Bamberger and Hoffmann (this vol., i, 139) in support of the centric formulæ as an explanation of the hydrogenation phenomena in anthracene derivatives is criticised. The phenomena there cited depend, according to the author, upon the peculiar constitution of the central benzene nucleus. The constitution of other cycloïd systems is also discussed from the point of view of centric formulæ.

The deductions which Stohmann draws from his calorimetric determinations (*Sächs. Ges. Wissensch.*, 1893, 477; also this vol., ii, 80) as to the constitution of benzene (compare also, Brühl, this vol., i, 366), are regarded by the author as premature. The author also refers to Schöpff's work on phenonaphthacridine (this vol., i, 41), which, he contends, furnishes no evidence against his views.

The following experiments are brought forward by the author as a fresh support of Körner's quinoline formula :—α-Amidolepidine (Ephraim, Abstr., 1892, 1488) boils at 320° undecomposed. When treated according to the Skraup or Doebner-Miller methods, the greater portion remains unaltered.

γ-Amidoquinaldine (Ephraim, Abstr., 1893, i, 727) melts at 162—163°, and boils at 333°; the *platinochloride* melts at 223° with decomposition; and the *picrate* melts at 197—199°.

α-Methyl-γ-quinoquinoline, $C_{13}N_2H_{10}N \begin{cases} C_6H_4 \cdot C \cdot N{=}CH \\ CMe \cdot C \cdot CH{:}CH \end{cases}$, is obtained from γ-amidoquinaldine or its salts by Skraup's method; it forms small, yellowish crystals, melts at 206°, and boils undecomposed

above 360°. The *platinochloride* becomes brown at 250° without melting, and the *picrate* melts at 243°.

aa-*Dimethyl-γ-quinoquinoline*, $N\!\!<\!\!{}^{C_6H_4 \cdot C \cdot N = CMe}_{CMe \cdot C \cdot CH:CH}$, is prepared from

γ-amidoquinaldine by the Doebner-Miller method; it crystallises in long, felted needles, melts at 104°, and boils undecomposed above 360°; the *platinochloride* decomposes without melting above 200°; and the picrate sinters together and decomposes at 225°.

A. R. L.

Condensation Products of Aromatic Hydrazides of Ethylic Acetoacetate. Indole and Pyrazole Derivatives. By C. WALKER (*Amer. Chem. J.*, **16**, 430—442).—In preparing these hydrazides there is a great tendency towards the separation of alcohol and formation of pyrazolones; this, however, is in great measure prevented if the ethereal salt is added to the hydrazine dissolved in a little absolute ether, instead of the hydrazine being, as is usual, added to the salt.

Ethylic paratolyl-α-methylindole-β-carboxylate,

$$NH\!\!<\!\!{}^{C_6H_4Me}_{-\!\!-CMe}\!\!>\!\!C \cdot COOEt,$$
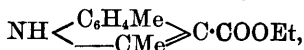
is formed by the action of strong sulphuric acid on ethylic aceto-acetate paratolylhydrazide. It crystallises in regular octahedra and tetrahedra, melts at 163—163·5°, and is readily soluble in alcohol, ether, benzene, and acetone. It gives the indole splinter reaction, and when heated with potash at 150° yields the dimethylindole described by Raschen (Abstr., 1887, 956). *Ethylic acetoacetate orthotolylhydrazide* is crystalline, melts at 95—97°, and is soluble in the usual organic solvents. *Ethylic orthotolyl-α-methylindole-β-carboxylate* forms monoclinic prisms melting at 173° and soluble in alcohol and ether. Whilst hydrazides of substituted ethylic acetoacetates yield with sulphuric acid a certain amount of the indole derivatives, the main products of the reaction are pyrazolonesulphonic acids, more of the latter being formed the higher the temperature of the reacting compounds.

Ethylic α-indolepropionate, $C_6H_4\!\!<\!\!{}^{CH}_{NH}\!\!>\!\!CHMe \cdot COOEt,$ from ethylic methylacetoacetate phenylhydrazide, forms white crystals melting at 136°, is soluble in organic solvents, and gives the indole splinter reaction. *Phenyldimethylpyrazolone-sulphonic acid,*

$$\substack{CO-NPh \\ CMe:CMe}\!\!>\!\!N \cdot SO_3H \ (?),$$
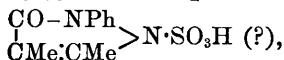
crystallises from boiling water in white needles, is sparingly soluble in all solvents, and is still solid at 300°. It gives Knorr's pyrazoline reaction. With ethylic ethylacetoacetate phenylhydrazide, the sulphuric acid indole reaction seems to proceed differently, ethylamine being separated, and the same ethylic α-methylindole-β-carboxylate produced as is formed by the action of sulphuric acid on ethylic aceto-acetate phenylhydrazide (Abstr., 1893, i, 368). 1-*Phenyl-3-methyl-4-benzyl-5-pyrazolonesulphonic acid,* formed by the action of strong

sulphuric acid on the phenylhydrazide of ethylic benzylacetoacetate, crystallises in white flakes, easily soluble in hot benzene or chloroform, more sparingly in alcohol. It is still solid at 300°, forms stable salts which are non-crystallisable, and gives Knorr's pyrazoline reaction. Attempts to eliminate the sulphonic group so as to form phenylmethylbenzylpyrazolone were unsuccessful, although the above sulphonic acid was reproduced by sulphonating the latter pyrazolone. 1-*Orthotolyl-3-methyl-5-pyrazolone*, obtained by the spontaneous decomposition of ethylic acetoacetate orthotolylhydrazide at ordinary temperatures, forms quadratic prisms or needles melting at 143—144°. 1-*Phenyl-3-methyl-4-benzyl-5-pyrazolone* forms glistening scales melting at 136°. It is readily soluble in alkali, sparingly in boiling water.

Phenylmethylethoxypyrazole (*loc. cit.*) is best obtained by the action of acetic chloride on an ethereal solution of the hydrazide at very low temperatures (−15°). It crystallises in hexagonal prisms or needles, melts at 68—68·5°, is insoluble in water but soluble in organic solvents. It gives Knorr's pyrazoline reaction, but does not give a coloration with ferric chloride. When heated with alcoholic potash, it yields *phenylmethylhydroxypyrazole*, which is readily soluble in alkalis and in organic solvents, crystallises in orange needles, and melts at 196—198°. It gives no coloration with ferric chloride, but Knorr's reaction gives a permanent green coloration. Its salts are tolerably stable, and are mostly soluble in water.　　　　　　L. T. T.

Isopyrazolones. By S. RUHEMANN (*Ber.*, **27**, 1658—1663).— When ethylic dicarboxyglutaconate, $CH(COOEt)_2 \cdot CH:C(COOEt)_2$, is mixed with excess of hydrazine hydrate, there are formed ethylic isopyrazolonecarboxylate, its hydrazine salt, malonylhydrazide, and ethylic malonate; the split thus takes place between the two CH groups. Ethylic methyldicarboxyglutaconate reacts in a similar manner. *Malonylhydrazide*, $CH_2(CO \cdot NH \cdot NH_2)_2$, melts at 154°. *Ethylic isopyrazolonecarboxylate*, $\begin{smallmatrix} NH \cdot CH \\ NH \cdot CO \end{smallmatrix} \!\!> \!\! C \cdot COOEt$, melts at 180—181°; its *hydrazine* salt, $C_6H_8N_2O_3,N_2H_4$, softens at 140°. It forms a *diargentic* salt which, when boiled with methyl iodide, yields *ethylic dimethylisopyrazolonecarboxylate*, $\begin{smallmatrix} NMe \cdot CH \\ NMe \cdot CO \end{smallmatrix} \!\!> \!\! C \cdot COOEt$, melting at 88—89°. It is further hydrolysed by boiling with aqueous potash, and, on acidifying the solution, white *isopyrazolonecarboxylic acid* is precipitated. This, however, is unstable, and is converted by boiling water into *isopyrazolone*, $\begin{smallmatrix} NH \cdot CH \\ NH \cdot CO \end{smallmatrix} \!\!> \!\! CH$, which melts at 165°. It will be noticed that displacement of the H in the NH groups in isopyrazolone and its derivatives produces a lowering of the melting point.　　　C. F. B.

Conversion of Thiocumazone into Thioquinazolines. By C. PAAL and O. COMMERELL (*Ber.*, **27**, 1866—1870).—Thiocumazone (Abstr., 1893, i, 25) reacts with primary aromatic bases to form thioquinazolines, identical with those described by Busch (Abstr., 1892,

1495; this vol., i, 146). Aniline, for example, produces 3-(n)-phenyl-tetrahydro-2-thioquinazoline, melting at 260°. This reaction serves as an additional proof of the formula already adopted for thiocumazone.

When reduced in alcoholic solution with metallic sodium, thiocumazone is quantitatively converted into orthotoluidine.

A. H.

Dithiourazole and its Derivatives. By M. FREUND (*Ber.*, **27**, 1774—1775; see also this vol., i, 97).—Thiocarbamides of the type $R \cdot NH \cdot CS \cdot NH \cdot NH \cdot CS \cdot NH \cdot R$ decompose in two ways, yielding compounds $C_2H_2RN_3S_2$ or $C_2H_2R_2N_4S$.

The following compounds of the first type have been prepared:—*dithiourazole*, $C_2H_3N_3S_2$, m. p. 245°; *methyldithiourazole*, $C_2H_2MeN_3S_2$, m. p. 187°; *ethyldithiourazole*, m. p. 140°; *allyldithiourazole*, m. p. 130°; and *phenyldithiourazole*, m. p. 215°. These compounds are strong acids, yield crystalline salts, contain two nitroso-groups, and may be converted quantitatively into the corresponding azo-compounds.

The compounds of the second type have basic properties; the following have been prepared:—*Imidothiourazole*, $C_2H_2N_4S$, m. p. 210—212°; *methylimidomethylthiourazole*, $C_2H_2Me_2N_4S$, m. p. 177°; and *ethylimidoethylthiourazole*, m. p. 173°.

E. C. R.

Iodides of Narceïne. By G. B. FRANKFORTER (*J. Amer. Chem. Soc.*, **16**, 361—363).—The author has re-examined the iodides of narceïne. The *blue iodide* formed by treating crystals of narceïne directly with iodine has the formula $(C_{23}H_{27}NO_8)_3I_2 + 3H_2O$, forms prismatic needles slightly soluble in water, loses its water of crystallisation at 100°, and melts at 176—177°, or if rapidly heated at 180—181°. When narceïne is treated with alcoholic solution of iodine, a greyish-blue substance is formed, which, on exposure to air, or when gently heated, changes to a *red iodide* of the formula $(C_{23}H_{27}NO_8)_3I + 3H_2O$. At 100° it loses its water, forming a brick-red powder melting at 181°, and insoluble in water, alcohol, and ether. Both iodides, if just neutralised with soda, yield white, hexagonal prisms which are now under investigation.

L. T. T.

Merochinine and Cincholeupone. By W. KOENIGS (*Ber.*, **27**, 1501—1507; compare this vol., i, 392).—Merochinine, $C_9H_{15}NO_2$, is formed by the oxidation of cinchonine with potassium dichromate and sulphuric acid. When it is heated with dilute hydrochloric acid at 240°, a base of the formula $C_8H_{11}N$ is formed, the yield being considerably increased if an oxidising agent, such as mercuric chloride, be also present. This base appears to be identical with the β-collidine obtained by Oechsner de Coninck (*Ann. Chim. Phys.*, [5], **27**, 469). On oxidation, it yields two acids which are most probably cinchomeronic acid, $C_5H_3N(COOH)_2$, and homonicotinic acid, $C_5H_3MeN \cdot COOH$. The base derived from merochinine is, therefore, γ-methyl-β-ethylpyridine. Merochinine, like cincholeupone hydrochloride, when distilled with zinc dust, yields a small amount of β-ethylpyridine.

The mother liquor of apocinchine contains *dihydrocinchine,*

$C_{19}H_{22}N_2$, which may be crystallised from alcohol, and melts at 145°. Its *platinochloride* does not melt below 265°, whilst its *picrate* melts at 197°. Towards hydrobromic acid this base behaves in a different manner from cinchine itself, no elimination of ammonia occurring. Aqueous phosphoric acid at 170—180°, on the other hand, decomposes both bases in a similar way, lepidine being formed, accompanied by merochinine in the case of cinchine, and by cincholeupone in that of dihydrocinchine. The dihydrocinchine was probably derived from dihydrocinchonine contained in the original commercial cinchonine, and it is, therefore, probable that the cincholeupone, which is obtained by the oxidation of commercial cinchonine, is formed at the expense of the dihydrocinchonine present, and is not a direct oxidation product of pure cinchonine.

Dihydrocinchine is also decomposed by phosphoric acid, but the product which accompanies the lepidine has not yet been examined. The results so far obtained seem to show that merochinine contains an imido- and a carboxyl-group, and is derived from γ-methyl-β-ethylpyridine, and this throws some light on the structure of quinine and cinchonine. A. H.

Conhydrine and Pseudoconhydrine. By C. ENGLER and A. KRONSTEIN (*Ber.*, **27**, 1779—1784).—When pure pseudoconhydrine (m. p. 101—102°) is dissolved in an excess of boiling light petroleum, and ether added to the solution, a modification separates in large, transparent leaflets. The authors name this modification *b*-pseudoconhydrine, and the other modification (m. p. 101—102°) *a*-pseudoconhydrine.

b-*Pseudoconhydrine* melts at 52—69°. The crystals always contain minute drops of the solvent; but as the melting point is always the same, whatever solvent is employed, there is no doubt that a true modification is present. This modification is converted into *a*-pseudoconhydrine, on leaving it for some time over calcium chloride, on heating at 200°, on sublimation, or on crystallisation from a small quantity of light petroleum, ether, or chloroform. A microcrystallographic examination of the conversion of *b*-pseudoconhydrine into *a*-pseudoconhydrine shows that by cautiously warming the *b*-modification it is converted into an enantiotropic modification (*c-pseudoconhydrine*), which on cooling is reconverted into the *b*-form.

When *a*-pseudoconhydrine is boiled for some hours with light petroleum in a reflux apparatus, it is partially converted into conhydrine and *b*-pseudoconhydrine. The latter, when treated in a similar way, is partially converted into conhydrine and *a*-pseudoconhydrine.

The authors were unable to convert conhydrine into an isomeric modification by heating it with solvents. A negative result was also obtained with α-ethylpiperylalkaline. E. C. R.

Preparation of Cocaïne from the Allied Alkaloïds. By A. EINHORN and R. WILLSTÄTTER (*Ber.*, **27**, 1523—1524).—This has hitherto been carried out by treating the alkaloïds with concentrated hydrochloric acid, so as to obtain ecgonine, and then preparing

cocaïne from this by converting it into the benzoyl-derivative, followed by etherification. A simpler plan is to heat the alkaloïds with methylic alcohol and sulphuric acid, or in a current of hydrogen chloride ; in this case the methylic ether of ecgonine is directly obtained, and merely requires to be converted into the benzoyl compound. If ethylic alcohol is employed, the ethylic ether of ecgonine is obtained.

A. H.

Canadine: A Third Alkaloïd from the Root of Hydrastis Canadensis. By E. SCHMIDT (*Arch. Pharm.*, **232**, 136—154).—The existence of a third alkaloïd in *Hydrastis canadensis* has not been hitherto clearly proved. The author, by taking advantage of the slight solubility in cold water of its nitrate, has isolated a new alkaloïd from this source, in addition to berberine and hydrastine.

Canadine, $C_{20}H_{21}NO_4$, was obtained in colourless needles, which become yellow on exposure to light, and melt at 132·5°. With the exception of the sulphate, its salts with inorganic acids are characterised by their sparing solubility. An alcoholic solution of canadine is neutral to litmus, and is strongly lævogyrate, this property also belonging to aqueous solutions of its salts. The alkaloïd dissolves in nitric acid with production of a yellow colour, whilst with vanadic anhydride and sulphuric acid it gives an olive-green, changing to brownish-black. Erdmann's reagent and Fröhde's reagent develop a transient olive-green coloration, which rapidly becomes brownish-red ; a bluish-green colour, due to the formation of Prussian blue, is produced when the solution of a canadine salt is added to a mixture of potassium ferricyanide and ferric chloride.

The *sulphate*, $C_{20}H_{21}NO_4,H_2SO_4$, crystallises in large, colourless plates, associated with varying quantities of yellow needles, consisting of $C_{20}H_{21}NO_4,H_2SO_4 + H_2O$. The *hydrochloride* and *nitrate* are colourless salts which are only sparingly soluble in cold water. The *platinochloride, aurochloride*, and *methiodide* have been prepared and analysed, the latter forming pale yellow crystals melting at 228—232° ; moist silver oxide converts the methiodide into an alkaline compound, which yields a *platinochloride* of the formula $(C_{20}H_{20}HNO_4)_2,Me_2PtCl_6$.

Canadine, when heated in alcoholic solution with iodine, is converted into berberine hydriodide. This reaction, coupled with the fact that berberine sulphate is present in solutions of canadine sulphate which have been exposed to light and air, suggests the probability of canadine being a tetrahydroberberine, isomeric with hydroberberine, the isomerism between these compounds depending on the different positions in the berberine molecule which it is possible for hydrogen atoms to assume. M. O. F.

Oxidation of Proteïds by Potassium Permanganate. By S. BONDZYŃSKI and L. ZOJA (*Zeit. physiol. Chem.*, **19**, 225—238).—Maly described, as the product of oxidation of egg-white by potassium permanganate, a substance, oxyprotosulphonic acid (Abstr., 1885, 824), in which the amounts of carbon and nitrogen are approximately in the same proportion as in albumin. In the present research, this substance was prepared from pure proteïds—crystals of egg-albumin and

of oxyhæmoglobin. In the case of caseïn, which differs from albumin in containing phosphorus in its molecule, the results of analysing fractions of the oxidation product show it to consist of two substances. W. D. H.

Crystallised and Ash-free Albumin. By E. HARNACK (*Zeit. physiol. Chem.*, **19** 299—300).—Polemical. The author states that he has never cast aspersions or doubts on Hofmeister's work on crystalline egg-albumin, as Bondzyński and Zoja consider. He only adheres to his previous statement, that his ash-free albumin forms a crystalline compound with ammonium sulphate which is poor in proteïd and rich in ammonia. W. D. H.

Proteïds of Egg-White. By R. T. HEWLETT (*Proc. physiol. Soc.*, 1894, 9—12).—The so-called globulin of white of egg gives most of the reactions of nucleo-albumin, but phosphorus determinations have yet to be made to confirm the supposition.

With regard to the albumin, not only does fractional heat coagulation suggest the presence of two or more proteïds, but fractional precipitation by ammonium sulphate tends in the same direction; moreover, some of the fractions are precipitated by both normal and tribasic lead acetate, others only by the latter.

Ramsden found that prolonged heating for days brings down albumins at temperatures considerably below their usual coagulation point. If thymol had been used as an antiseptic in these experiments, a source of error was introduced, as this substance and, to a less degree, camphor precipitate proteïds slowly. W. D. H.

Albumone. By R. BRUNNER (*Inaug. Diss. Bern.*, 1894).—Chabrié (Abstr., 1892, 224) prepared from human blood serum a new proteïd he called albumone. Ox blood, by similar treatment, yields the same substance. It does not, however, pre-exist in the serum, and the present research shows that it is formed during the process of heat coagulation, partly from serum-albumin, partly from serum-globulin. W. D. H.

Specific Rotatory Power of Fibrinogen. By F. MITTELBACH (*Zeit. physiol. Chem.*, **19**, 289—298).—Hammarsten states that on heating a solution of fibrinogen to 56°, a globulin is split off from it which coagulates at 65°. The present research does not confirm this, and Hammarsten's result is explained in the same way that Haycraft explains the result of fractional heat coagulation generally. Great dilution raises the temperature of heat coagulation of fibrinogen to 65°, and dilution would occur if the greater part of the proteïd were coagulated at 56° and removed by filtration. The specific rotatory power is given as $(\alpha)_D = -52.5°$. Hermann (Abstr., 1887, 1131) gives $-43°$. W. D. H.

Organic Chemistry.

Relationships between Boiling Points, and between Melting Points. By G. COHN (*J. pr. Chem.*, [2], **50**, 38—57).—The author calls attention to relationships which exist between the boiling points of (1) orthodiketones; (2) ketones and the acids from which they are derived in the manner indicated by the equation $RCOOH + R'COOH = RCOR' + H_2CO_3$; (3) aldehydes and the acids formed by their oxidation; (4) ethers and the alkyl haloïds and hydroxides from which they are derived in accordance with the equation $RCl + R'OH = HCl + RR'O$; (5) amines and aldehydes, an examination of which shows that the amines have approximately the same boiling points as have the aldehydes containing the same number of carbon atoms; (6) saturated and unsaturated compounds containing the same number of carbon atoms; these show approximately the same boiling points; (7) aromatic compounds containing COOH on the one hand, and those containing C_6H_5 in place of this COOH on the other hand; these have approximately the same boiling points; (8) methyl ketones, methylic salts, and chloranhydrides; these have approximately the same boiling points. Relationships between melting points are less marked; the author calls attention to several cases of these in conclusion (compare Schröder, Abstr., 1883, 990; Baeyer, Abstr., 1878, 3; Kipping, Trans., 1893, 465). A. G. B.

Action of Heat on Ethylene. By V. B. LEWES (*Proc. Roy. Soc.*, **55**, 90—107).—The action of heat on ethylene was studied at temperatures ranging from 600° to 1500°, the gas being passed through a platinum tube of 2 mm. bore heated through a length of 140 mm. Incidentally, the behaviour, under similar circumstances, of ethane, acetylene and methane, and of benzene vapour was investigated. The author concludes that, taking into consideration the complexity of the changes involved and the difficulty in obtaining great accuracy in gas analysis, these results seem to prove that the primary action of heat on ethylene may be represented by the equation $3C_2H_4 = 2C_2H_2 + 2CH_4$, whilst the final decomposition is that represented by previous observers, namely, $C_2H_4 = C_2 + 2H_2$; between these two extremes there occur a large number of interactions due to the polymerisation of the acetylene formed from the ethylene, and also at higher temperatures from the methane in accordance with the equation $2CH_4 = C_2H_2 + 3H_2$. C. F. B.

Preparation of Tetrachlorethylene and its Oxidation by Ozone. By A. BESSON (*Compt. rend.*, **118**, 1347—1350).—The action of metals on carbon tetrachloride is either too slow and yields only C_2Cl_6, or, at higher temperatures, becomes explosive, with liberation of carbon. Aluminium foil acts slowly, and the filings act very rapidly, especially in presence of iodine, but no useful quantity of

tetrachlorethylene is formed. The action of ordinary phosphorus becomes explosive at 200°, and that of red phosphorus is very slow even at 300°.

When hydrogen mixed with vapour of carbon tetrachloride is passed through a tube containing pumice heated to redness, decomposition takes place with incandescence and separation of carbon. At a temperature below redness the action is less violent, and the chlorides, $CHCl_3$, CH_2Cl_2, C_2Cl_6, and C_2Cl_4 are obtained. With very porous pumice, and a temperature just below that at which separation of carbon begins, the yield of tetrachlorethylene may amount to as much as 10 per cent. of the original carbon tetrachloride.

Ozone acts very slowly on tetrachlorethylene at 0°, but at 30° oxidation takes place, and a small quantity of carbon oxychloride is given off. The chief product of oxidation is trichloracetic chloride, $CCl_3 \cdot COCl$, which, with water, yields hydrochloric and trichloracetic acids. From this result it would seem that tetrachlorethylene should be represented by the formula $CCl_3 \cdot CCl$. Careful fractionation, however, gives no evidence of the existence of two isomeric tetrachlorethylenes. It is noteworthy that Prud'homme has previously obtained trichloracetic chloride by the oxidation of tetrachlorethylene by sulphuric anhydride at a temperature above 100°.

Tetrachlorethylene oxide, $(CCl_2)_2O$, seems, however, to be formed by the action of ozone, especially if the temperature does not exceed 10°. It boils at about 110° under a pressure of 20 mm., is insoluble in, and is not attacked by, water, and has a disagreeable odour. When exposed to air, it explodes at its boiling point. The quantity obtained was not sufficient for a complete analysis, but the proportion of carbon corresponds with the formula given.   C. H. B.

Action of Bromine on Diallyl. By K. KRASUSKY (*J. Russ. Chem. Soc.*, **25**, 619—626).—If, in Berthelot and De Luca's method of preparing diallyl from allylic iodide and sodium, a copper flask is substituted for a glass one, the yield obtained rises to 87 per cent. of the theoretical.

Bromine was added drop by drop at 0° to an ethereal or chloroform solution of diallyl prepared in this way until it was permanently coloured. After the mixture had been left for 10 hours in the dark, the solvent was evaporated and the solid part of the residue separated from the comparatively small liquid part, which did not solidify in a freezing mixture. The liquid portion was dissolved in alcohol and fractionally precipitated by the addition of successive small quantities of water. The first portions precipitated, solidified on standing. The fractions which remained liquid were separated, dried, and distilled under 19 mm. pressure, fractions being collected at various temperatures between 100° and 180°, and the quantity of bromine in them determined. The bromine in the solid portions corresponded with the formula of the tetrabromide, $C_6H_{10}Br_4$; but the liquid portions always contained much less bromine than the tetrabromide, so that the conclusion of Ciamician and Anderlini, that the liquid is a stereoisomeride of the solid tetrabromide, is incorrect.   J. W.

Chlorination of Alcohol. By P. FRITSCH (*Annalen*, **279**, 288—300).—According to Lieben (*Annalen*, **104**, 114; *Ber.*, **3**, 907), the action of chlorine on alcohol is, first of all, to produce aldehyde, which then reacts with 2 mols. of alcohol to form acetal; the further action of chlorine on this substance yields trichloracetal, which is then decomposed into chloral alcoholate and ethylic chloride by the hydrogen chloride formed. The author's experiments show that when chlorine is passed into alcohol, the first product which can be isolated is monochloracetal. As the chlorination proceeds beyond this point, increasing amounts of dichloracetal are produced, and these two compounds are partially converted, by the hydrogen chloride formed, into di- and tri-chlorether respectively. This is shown by the fact that if a litre of alcohol be treated with 500 grams of chlorine, the hydrogen chloride removed by digestion with marble, and water added, only 100 grams of the mixed chloracetals are obtained, whilst if half a volume of alcohol be added before the treatment with marble, 210 grams of the chloracetals are obtained, the difference being the amount formed by the interaction of the alcohol with the chlorinated ether present.

If the temperature is maintained at 25—30°, and the chlorination continued, a heavy oil separates, and, finally, the chlorine ceases to be absorbed. This heavy layer (sp. gr. 1·32) consists chiefly of trichlorether, $CHCl_2 \cdot CHCl \cdot OEt$, along with smaller quantities of dichlorether and the hydrates of mono- and di-chloraldehyde. When this oil is distilled, the di- and tri-chlorethers are partially converted by the water present into the alcoholates of the corresponding chlorinated aldehydes, which then decompose on distillation, with evolution of hydrogen chloride, into water, chlorinated aldehydes, and chlorinated acetals.

The lighter layer of liquid (sp. gr. 1·2) is a concentrated solution of hydrogen chloride containing a small amount of dichloraldehyde.

If the temperature be now raised to about 42—45° and the chlorination again continued, a homogeneous liquid is obtained, the trichlorether being converted by the aqueous solution into dichloraldehyde alcoholate, which is then finally converted by chlorination into chloral alcoholate, the mono- and di-chloraldehyde being at the same time converted into chloral.

The course of the whole reaction may therefore be expressed by the following equations.

$$(1.) \quad 3C_2H_6O + 2Cl_2 = CH_2Cl \cdot CH(OEt)_2 + 3HCl + H_2O.$$

$$(2.) \quad \begin{array}{l} CH_2Cl \cdot CH(OEt)_2 + Cl_2 = CHCl_2 \cdot CH(OEt)_2 + HCl. \\ CHCl_2 \cdot CH(OEt)_2 + HCl = CHCl_2 \cdot CHCl(OEt) + EtOH. \end{array}$$

$$(3.) \quad \begin{array}{l} CHCl_2 \cdot CHCl(OEt) + H_2O = CHCl_2 \cdot CH(OEt) \cdot OH + HCl. \\ CHCl_2 \cdot CH(OEt) \cdot OH + Cl_2 = CCl_3 \cdot CH(OEt) \cdot OH + HCl. \end{array}$$
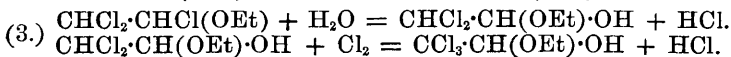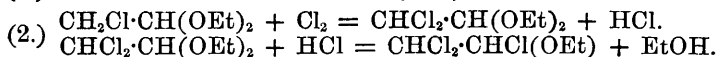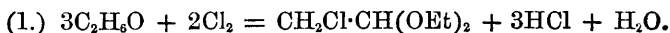
The liquid obtained by Liebig (*Annalen*, **1**, 221) by passing chlorine into cold alcohol, adding water, and thoroughly washing the oil with water, which was termed by him "heavy hydrochloric ether," is, in reality, a mixture of trichlorether with mono- and di-chloracetal.

In order to prepare monochloracetal, about 400—450 grams of chlorine is passed into a litre of alcohol of 94—99 per cent. at 25°

(until the specific gravity of the liquid is 1·02—1·03), $\frac{1}{2}$ litre of alcohol is added, the whole heated to 50—60°, digested with marble, precipitated with water, and fractionated. The yield amounts to about 200 grams. Dichloracetal may also be readily prepared by passing chlorine into a litre of alcohol at a temperature of 25—30° as long as it is easily absorbed; a litre of alcohol is then added to the heavy layer which has been formed, the whole digested with marble, and the oil which is precipitated on adding water fractionated; about 850—900 grams are obtained. A. H.

Mechanism of the Action of Chlorine on Isobutylic Alcohol.

By A. BROCHET (*Compt. rend.*, **118**, 1280—1282).—Chlorine is rapidly absorbed by isobutylic alcohol at the ordinary temperature, and the liquid must be cooled. The chief product is unsymmetrical *dichlorisobutylic oxide*, $CMe_2Cl·CHCl·O·CH_2·CHMe_2$, a refractive, very mobile liquid which boils at 192·5° under a pressure of 760 mm., and at 83° under a pressure of 15 mm.; $d\ 15°/4° = 1·031$; refractive index, $n_{19} = 1·437$. It has a pleasant ethereal odour when freshly distilled, but, when exposed to moist air, decomposes slightly, with evolution of hydrogen chloride. It seems probable that the action of chlorine on isobutylic alcohol first produces α-chloroisobutaldehyde, and the latter condenses with the unaltered alcohol in presence of the hydrochloric acid that is formed simultaneously.

Water has little action on dichlorisobutylic oxide at the ordinary temperature, but at 100° decomposes it rapidly with evolution of hydrogen chloride and formation of α-chlorisobutaldehyde and diisobutylmonochlorisobutyral, $CMe_2Cl·CH(OC_4H_9)_2$. Alkali hydroxides and calcium and barium hydroxides induce a similar decomposition. Isobutylic alcohol, at its boiling point, and sodium ethoxide or sodium isobutyloxide, at the ordinary temperature, also give rise to the same products. Diisobutylmonochlorisobutyral has an agreeable odour and boils at 218°; $d\ 15°/4° = 0·9355$; refractive index, $n_{17} = 1·426$. When heated with acetic anhydride in a sealed tube, it yields α-chlorisobutaldehyde and isobutylic acetate. When mixed with ethylic carbamate and saturated with hydrogen chloride, it yields chlorisobutylideneurethane identical with that obtained by the direct action of the aldehyde. C. H. B.

Preparation of Methylic Nitrate.

By G. BERTONI (*Chem. Centr.*, 1894, i, 623—624; from *Boll. chim. farmac.*, **33**, 33).—Methylic nitrate may be safely prepared as follows: 160 grams of dried and finely-powdered ammonium nitrate is introduced into a tubulated retort, and a mixture of 100 grams of methylic alcohol with 100 grams of sulphuric acid allowed to flow in. The retort is then at once placed in a water bath at 100° (without a flame), when the colourless nitrate distils over, and should be washed with water and dried over calcium chloride. L. T. T.

Ethylphosphoric acid.

By J. CAVALIER (*Compt. rend.*, **118**, 1275—1277).—The heat of neutralisation of ethylphosphoric acid, H_2EtPO_4, by successive equivalents of different alkalis, is as follows.

	Sodium hydroxide.	Potassium hydroxide.	Ammonia.	Barium hydroxide.
1st Equivalent..	15·59	15·73	14·44	16·30
2nd ,, ..	13·80	13·61	12·03	13·88
3rd ,, ..	0·86	0·85	0·53	0·18

It is obvious that ethylphosphoric acid behaves as if it had two distinct acid functions analogous to those of the oxy-acids of phosphorus, although the difference in thermal value between the first and second functions is less strongly marked.

With one equivalent of alkali, the solutions are neutral to methyl-orange; with two equivalents they are neutral to phenolphthaleïn; methyl-orange, therefore, serves as a useful indicator for the preparation of the acid salts of the general formula $MHEtPO_4$. The sodium compound forms a crystalline deliquescent mass; the potassium salt is also crystalline and very deliquescent; the ammonium salt forms transparent crystals which alter but little when exposed to air. The barium salt crystallises with $1H_2O$ in nacreous plates which are stable when exposed to air, and the calcium and strontium salts are also crystalline. All these salts when heated at about 300° give off alcohol and are converted into pyrophosphates, but their solutions are stable, and are not affected by prolonged ebullition. The calcium salt, unlike the corresponding phosphate, is not partially decomposed by water, and its aqueous solution remains neutral and yields no precipitate when boiled.   C. H. B.

Chlorination of Ether. By P. FRITSCH and W. SCHUMACHER (*Annalen*, **279**, 301—310; compare this vol. i, 483).—When chlorine is passed into cooled ether, the first product is monochlorether, which cannot, however, be obtained in the pure state, as it decomposes very rapidly on distillation. The final product of the action of chlorine on ether at 15°, when distilled under diminished pressure, yields two main fractions, one of which boils at 80—81°, and the other at 102—103°, under a pressure of 100 mm. The first consists chiefly of dichlorether, the second of trichlorether; but neither is pure, and cannot be obtained pure even by repeated distillation, as a certain amount of decomposition always occurs.

Dichlorether is readily decomposed by water at the ordinary temperature (compare Abeljanz, *Annalen*, **164**, 222), and, if the hydrochloric acid be removed by digestion with marble, 90 per cent. of the theoretical amount of monochloraldehyde alcoholate is obtained. On distillation, this substance decomposes into monochloraldehyde, water, and monochloracetal; $2CH_2Cl\cdot CH(OEt)\cdot OH = CH_2Cl\cdot CHO + H_2O + CH_2Cl\cdot CH(OEt)_2$. It may advantageously be used for the preparation of monochloraldehyde, which is formed to the extent of 90 per cent. of the theoretical yield, when the alcoholate is heated with anhydrous oxalic acid. When it is treated with alcohol, the alcoholate yields monochloracetal. If methylic alcohol be added, a mixture of the dimethyl- and diethyl-acetals is obtained, and not a mixed acetal.

Trichlorether is only very slowly attacked by cold water, yielding

dichloraldehyde alcoholate; on distillation, this decomposes into dichloraldehyde hydrate and dichloracetal, but not so sharply as the monochloro-compound. Dichloraldehyde alcoholate may also be employed for the preparation of dichloraldehyde and dichloracetal.

A. H.

Cholesterol. By J. MAUTHNER and W. SUIDA (*Monatsh.*, **15**, 362—374).—A great number of analytical results obtained by the authors with cholesterol and its derivatives, seem to show that the composition of cholesterol is expressed by the formula $C_{27}H_{44}O$.

The compound obtained by treating trichlorocholestane with zinc-dust and acetic acid, and also by the action of zinc acetate on cholesterylic chloride, is found to be cholesterylic acetate. Cholesterylic proprionate and butyrate may be obtained from cholesterylic chloride in a similar way. The propionate melts at 97—98°. E. C. R.

A Polymeride of Epichlorhydrin. By E. PATERNÒ and V. OLIVIERI (*Gazzetta*, **24**, i, 305—309).—Epichlorhydrin (200 c.c.) is slowly added to concentrated hydrofluoric acid (20 c.c.) contained in a platinum vessel; after 24 hours' repose, the product is rendered slightly alkaline by the addition of sodium carbonate, and any excess of epichlorhydrin is carried away by a current of steam. The residual oil, which is more viscous than glycerol, is a *polymeride* of epichlor-hydrin; it has a piquant odour, is heavier than water, and dissolves in alcohol, benzene, ether, or acetic acid. It decomposes at 200° when distilled under diminished pressure, and gives anomalous depressions of the boiling point of benzene. No oxime or hydrazone could be prepared, but the substance is acted on by acetic chloride or an-hydride. It also yields a *product* resembling cellulose, when heated at 200° with very dilute sulphuric acid; this substance, however, could not be isolated in a pure state. W. J. P.

Behaviour of Various Sugars towards Pure Yeast Cultures.— By E. FISCHER and H. THIERFELDER (*Ber.*, **27**, 2031—2037).—No systematic attempt has hitherto been made to study the behaviour of synthetical sugars towards pure cultures of yeast. The authors, following this line of investigation, have also reopened the study of a few natural sugars, employing in their experiments the following twelve varieties of yeast: *Saccharomyces pastorianus*, I, II, III; *S. cerevisiæ*, I; *S. ellipsoideus*, I, II; *S. marxianus; S. membranæfaciens; S. productivus;* and three forms known as "brewery yeast," "distil-lery yeast," and "milk-sugar yeast" respectively. Repetition of previous experiments has invariably led to the confirmation of re-corded conclusions, except in the case of sorbose, which is not attacked by pure cultures.

The experiments were carried out in a flask of about 1 c.c. capacity, into the neck of which a small U-tube is fitted. The flask having been two-thirds filled with a mixture of yeast extract containing citric acid, and a 20 per cent. solution of the sugar under examination, the liquid is sterilised, and 0·013 gram of the pure culture introduced; the U-tube containing baryta water is then fitted into the neck of the flask, special attention being paid to the security of the joint. The

whole apparatus is then allowed to remain at 24—28° for a period of from 3 to 10 days.

The authors have succeeded in tracing a connection between the molecular configuration of a sugar and its behaviour towards ferments, pointing out that whilst grape-sugar and d-mannose are readily fermentable, a selective capacity is displayed by the cultures towards d-galactose and d-talose, the former being only slowly attacked by some yeasts, d-talose escaping altogether. The delicacy of this discrimination between geometrical modifications is rendered more striking by the fact that such widely dissimilar molecular arrangements as glycerose and mannononose are broken down by these organisms; it seems probable that the yeasts attack with most readiness those sugars whose molecular configuration resembles most closely that of grape sugar.

In addition to the sugars already mentioned, it is found that the cultures have no action on l-mannose, l-gulose, l-arabinose, rhamnose, α-glucoheptose, or α-glucooctose. Representatives of the glucosides recently described by E. Fischer (this vol., i, 3) have been included in the experiments, with the result that whilst *S. pastorianus* I, " brewery yeast," and " distillery yeast " induce fermentation in solutions of methyl- and ethyl-glucosides, no action is set up in the case of glucose-resorcinol, glucose-pyrogallol, or glucose-ethylmercaptol; this cannot be accounted for by the liberation of the aromatic residue and its subsequent action on the yeast, the latter preserving for many days its activity in a solution of grape sugar.

It was thought possible that by allowing growing yeast to remain for some months in contact with an infermentable sugar, the yeast in question might develop a fermentative capacity for that sugar; an experiment in this direction, however, led to a negative result.

M. O. F.

Action of Paraformaldehyde (Trioxymethylene) on Alcohols in presence of Ferric Chloride. By A. TRILLAT and R. CAMBIER (*Compt. rend.*, **118**, 1277—1280).—When a mixture of paraformaldehyde and an alcohol in molecular proportion is boiled for a few hours with from 1 to 4 per cent. of anhydrous ferric chloride, an action takes place in accordance with the general equation $(CH_2O)_3 + 6ROH = 3CH_2(OR)_2 + 3H_2O$. The products, which are obtained in considerable quantity, are colourless liquids with a very agreeable odour; the higher terms are insoluble in water, but form hydrates. They boil undecomposed under ordinary pressure. The propyl compound and its higher homologues dissolve sulphur and iodine. All the derivatives are violently oxidised by nitric acid, and react energetically with chlorine and bromine. Sulphuric acid decomposes them with regeneration of paraformaldehyde. Their characteristic reaction is the formation of coloured products with dimethylaniline in presence of an acid and an oxidising agent.

Methylal is readily obtained by this method from paraformaldehyde and methylic alcohol. The ethyl compound is obtained as a hydrate, $CH_2(OEt)_2 + H_2O$ boiling at 74—75°; sp. gr. at 16° = 0·8338; 1 part dissolves in 15 parts of water at 20°. The normal propyl compound has an odour of pine apple, and boils at 136°; sp. gr. at 14° =

0·8319. Its hydrate, with $1H_2O$, boils at 90°; sp. gr. at 14° = 0·8661. The isopropyl compound is obtained as a monhydrate which boils at 79—80°; sp. gr. at 14° = 0·8362. The isobutyl compound boils at 164°; sp. gr. at 14° = 0·8302. Its monhydrate boils at 96°; sp. gr. at 14° = 0·8491. The isoamyl compound boils at 206°; sp. gr. at 14° = 0·8391; its monhydrate boils at about 98°. The hexylic compound boils at 174—175°; sp. gr. at 15° = 0·8223. The caprylic compound boils at 289°, and is almost odourless; sp. gr. at 15° = 0·8477. The allyl compound has a pungent odour, and boils at 138—139°; sp. gr. at 14° = 0·8948; it forms a hydrate. The glycol compound, $CH_2(O\cdot CH_2\cdot CH_2\cdot OH)_2$, has a pungent odour, and boils at 74—75°; sp. gr. at 25° = 1·0534. With dimethylaniline, it gives the benzhydrol reaction. The propylglycol compound has a pleasant odour, and boils at 90°. C. H. B.

Condensation of Aldehydes with Cyanides. By C. BECHERT (*J. pr. Chem.*, [2], **50**, 1—28; compare Abstr., 1892, 1086).— *Methylenedisuccinimide*, $CH_2[N(CO)_2C_2H_4]_2$, is produced by the action between paraformaldehyde and ethylenic cyanide in glacial acetic acid, in the presence of strong sulphuric acid; it crystallises in monoclinic pyramids, and does not melt at 270°. Chromic and nitric acids are without action on the compound; nitrous acid has very little action on it, and bromine only attacks it when heated with it in presence of water; when it is distilled with dilute sulphuric acid, formaldehyde passes over, and succinic acid remains in the retort.

The interaction of ethylenic cyanide with benzaldehyde in alcohol at 0°, in presence of sodium ethoxide, yields a *compound*, $C_{21}H_{22}N_2O_2$, which crystallises in yellow needles, melting at 214°; its behaviour with hydrochloric acid indicates that it is a product of the condensation of 2 mols. of ammonia (produced from the ethylenic cyanide) with 3 of benzaldehyde.

When the action between ethylenic cyanide, benzaldehyde, and sodium ethoxide proceeds at 50°, *α-benzal-β-cyanopropionamide*, $CN\cdot CH_2\cdot C(CHPh)\cdot CO\cdot NH_2$, is produced. This crystallises from hot glacial acetic acid in white needles, carbonises at 260°, and is insoluble in most solvents.

Paramethoxybenzalsuccinamide,

$$OMe\cdot C_6H_4\cdot CH:C(CO\cdot NH_2)\cdot CH_2\cdot CO\cdot NH_2,$$
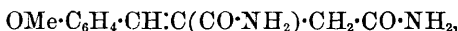
is formed on adding a hot solution of sodium ethoxide to a solution of ethylenic cyanide and anisaldehyde in alcohol; it crystallises in white needles, melts at 255°, and dissolves in alcohol and glacial acetic acid, but not in water or ether. It is feebly basic, yielding a *nitrate*, $C_{12}H_{14}N_2O_3,HNO_3$, which crystallises in yellow needles, and melts at 181°, and a *hydrochloride*, $C_{12}H_{14}N_2O_3,HCl$, which forms yellow needles melting at 240°.

Ethylic paramethoxyphenyl-α-cyanacrylate,

$$OMe\cdot C_6H_4\cdot CH:C(CN)\cdot COOEt,$$

the condensation product from ethylic cyanacetate and anisaldehyde, in presence of sodium ethoxide in alcoholic solution, forms pale

yellow, triclinic crystals, melts at 85°, and dissolves in alcohol, ether, chloroform, and benzene. The corresponding *acid* crystallises in yellow needles, and melts at 226° ; its *potassium* and *silver* salts were prepared, and the behaviour of the former with several of the usual precipitants is recorded. The ethylic salt, when treated with bromine in chloroform, yields the *bromo*-derivative,

$$OMe \cdot C_6H_4 \cdot CBr \vdots C(CN) \cdot COOEt ;$$
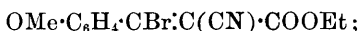
it crystallises in white needles, and melts at 185°. The acid does not yield this derivative.

Ethylic cinnamenyl-α-cyanacrylate, $CHPh \vdots CH \cdot CH \vdots C(CN) \cdot COOEt$, from cinnamaldehyde and ethylic cyanacetate in presence of sodium ethoxide, crystallises in yellow needles, melting at 114°. The corresponding *acid* forms red flocks, and melts at 196° ; the *potassium* salt and some of its reactions, and the *silver* salt, are described. The ethylic salt yields the *bromo*-derivative,

$$CHPhBr \cdot CHBr \cdot CH \vdots C(CN) \cdot COOEt,$$

which crystallises in white laminæ, and melts at 95° ; the corresponding derivative of the acid could not be prepared.

Ethylic furfur-α-cyanacrylate, $C_4OH_3 \cdot CH \vdots C(CN) \cdot COOEt$, is prepared in a similar manner ; it crystallises in white needles, melts at 94°, and dissolves in chloroform and alcohol. The corresponding *acid* crystallises in yellow needles, and melts at 218°. When the ethylic salt is brominated in glacial acetic acid, the *bromo*-derivative, $C_4OH_3 \cdot CBr \vdots C(CN) \cdot COOEt$, is obtained ; it crystallises in yellow needles, and melts at 111°. The acid yields no bromo-derivative.

Ethylic methylenedioxyphenyl-α-cyanacrylate,

$$CH_2 \vdots O_2 \vdots C_6H_3 \cdot CH \vdots C(CN) \cdot COOEt,$$
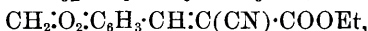
the condensation product formed from piperonal and ethylic cyanacetate in presence of sodium ethoxide, forms yellow laminæ, melting at 106° ; the corresponding *acid* crystallises in yellow needles, and melts at 230°. The *bromo*-derivative,

$$CH_2 \vdots O_2 \vdots C_6H_3 \cdot CBr \vdots C(CN) \cdot COOEt,$$
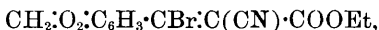
forms yellow crystals, melting at 131°.

Ethylic orthohydroxybenzaldicyanacetate,

$$OH \cdot C_6H_4 \cdot CH[CH(CN) \cdot COOEt]_2 + \tfrac{1}{2}H_2O,$$

prepared in like manner from ethylic cyanacetate and salicylaldehyde, forms white, hard, granular crystals, melts at 140°, and dissolves in the usual solvents. Its constitution is confirmed by the fact that, on treatment with ammonia, it yields the *imide*,

$$OH \cdot C_6H_4 \cdot CH {<}^{CH(CN) \cdot CO}_{CH(CN) \cdot CO} {>} NH,$$
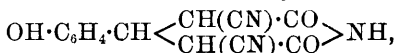
which crystallises in laminæ, does not melt at 280°, and is insoluble, except in glacial acetic acid. The *potassium* and *silver* salts of the corresponding acid were prepared, but when the yellow solution of the former is mixed with dilute sulphuric acid, a crystalline precipitate of *cyanocoumarin*, $C_6H_4 {<}^{O———CO}_{CH \vdots C(CN)} {>}$, is formed instead of

the free acid. This neutral substance melts at 182°, and gives no violet coloration with ferric chloride in alcoholic solution, showing that the salicylic hydroxyl no longer exists in the molecule; its constitution is further settled by the fact that it yields coumarincarboxylic acid (m. p. 187°) on hydrolysis. The same acid may be produced by the direct hydrolysis of ethylic orthohydroxybenzaldicyanacetate; its *barium* salt and *amide* (m. p. 236°) were prepared. With bromine, ethylic orthohydroxybenzaldicyanacetate yields a *bromo*-derivative, $C_{11}H_8NO_3Br_3$, as an orange-red crystalline powder, melting between 125° and 128°.　　　　　　　　　　　　　　　　　A. G. B.

Chlorination of Acetone. By P. FRITSCH (*Annalen*, **279**, 310—319; compare Abstr., 1893, i, 303).—When acetone is chlorinated in the usual way, the first product obtained has the boiling point ascribed to monochloracetone, but contains about 4 per cent. of chlorine less than is required for this substance, the deficiency being probably due to the presence of mesityl oxide, formed by the action of the accumulated hydrogen chloride on the excess of acetone. This impurity may be avoided by introducing 1 part of marble for every 4 parts of acetone into the chlorinating flask, and gradually dropping in $2\frac{1}{2}$ parts of water. The product thus obtained has the theoretical composition, boils at 118—120°, and has a sp. gr. of 1·154 at 15°.

The further chlorination of acetone, carried out in the same manner in diffused daylight, gave a product consisting of monochloracetone mixed with both asymmetric and symmetric dichloracetone. The last of these, which has not previously been recognised among the products of the direct chlorination of acetone (*Annalen*, **208**, 355; *Ber.*, **7**, 467), is found in the fraction which boils at 167—172°, and is formed to the extent of about 10 per cent. of the whole.

For the preparation of pentachloracetone, pure monochloracetone, or the crude mixture of mono- and di-chloracetone, may be used. The substance may thus be obtained in the pure state, free from condensation products or their chlorine substitution derivatives. Pentachloracetone has a sp. gr. of 1·69 at 15°, whereas, according to Cloëz (*Ann. Chim. Phys.*, [6], **9**, 189), who has also prepared it by direct chlorination, its sp. gr. is 1·576.　　　　　　　　　　　A. H.

Action of Ethylenediamine on Dicarboxylic acids. By F. ANDERLINI (*Gazzetta*, **24**, i, 397—401).—Ethylenediamine succinate melts and decomposes at 195°, not at the lower temperature given by Mason (Trans., 1887, **51**, 10).

Ethylenediamine malate, $C_2H_3(OH)(COOH)_2,(NH_2)_2C_2H_4$, is obtained by the action of malic acid on ethylenediamine; it forms small, colourless crystals, melting and decomposing at 198°.

The *phthalate* and *fumarate* are white, crystalline powders; they melt at 225—227° and 210° respectively, and at the same time undergo decomposition; the *maleate* was also prepared.　　　　　W. J. P.

Action of Ethylenediamine on Anhydrides of Bibasic acids. By F. ANDERLINI (*Gazzetta*, **24**, i, 401—407; compare this vol., i,

375).—Ethylenediamine and maleïc anhydride in benzene solution combine to form an additive *compound*, $C_2H_4(NH_2)_2,C_4H_2O_2$; it is a white, deliquescent powder, melting and decomposing at 90—110°.

The additive *product* of ethylenediamine and succinic anhydride is similar in appearance to the preceding; it melts and decomposes at about 120°, and resolidifies at 130—140°. This behaviour is due to the formation of *succinylethylenediamine*, $C_2H_4{<}^{NH\cdot CO}_{NH\cdot CO}{>}C_2H_4$, a white, hygroscopic substance, melting at 160—170°.

Phthalic anhydride also yields a similar additive *product* with ethylenediamine; on boiling with benzene, water is eliminated, and *phthalylethylenediamide*, $C_2H_4{<}^{NH\cdot CO}_{NH\cdot CO}{>}C_6H_4$, is formed. The latter is a voluminous, white, hygroscopic powder, melting at 125°.

Diphthalylethylenediimide, $C_6H_4{<}^O_O{>}N\cdot CH_2\cdot CH_2\cdot N{<}^O_O{>}C_6H_4$, is obtained by heating phthalic anhydride and ethylenediamine in benzene solution at 100°; it crystallises in colourless needles, melting at 243—244°, and distils without decomposing.　　　　W. J. P.

Oxidation of Normal Fatty Acids.

By R. MARGULIES (*Monatsh.*, **15**, 273—275).—The purity of the acids employed was proved by a determination of the boiling point and by the method of fractional saturation. Potassium permanganate was employed as the oxidising agent, both in acid solution and in alkaline. Acetic acid was found to be the most difficult to oxidise, and of the other fatty acids, those of higher molecular weight are more easily oxidised.

Acetic acid, in the presence of excess of sodium carbonate, yields carbonic and oxalic acids. In the presence of sulphuric acid, it yields only carbonic acid.

Propionic acid in alkaline solution yields oxalic acid; in acid solution, acetic acid.

Normal butyric acid in alkaline solution yields oxalic and acetic acids; in acid solution only acetic acid. Propionic acid could not be detected in the product. When oxidised with sodium peroxide in the cold, it yields acetic acid, and a small quantity of formic acid.

Normal heptylic acid, in alkaline solution, yields oxalic, acetic, and formic acids; in acid solution, acetic and traces of formic acid.

　　　　　　　　　　　　　　　　　　　　　　　E. C. R.

Action of Ammonium Hydrosulphide on Dichloracetic acid.

By C. BÖTTINGER (*Arch. Pharm.*, **232**, 244—248).—Dichloracetic acid (5 grams) is neutralised with ammonia, the solution cooled and mixed with saturated ammonium hydrosulphide solution (35 c.c.); after 60 hours, the mixture is evaporated on the water bath to expel excess of ammonium hydrosulphide, water is added and the solution is fractionally precipitated with lead acetate. The acids recovered from the first fraction consist of oxalic acid and the *acid* $C_2H_2SO_2 + H_2O$, which forms crystals, melts at 88—89°, and is much more soluble in water and in ether than oxalic acid is; the *lead* salt, the *silver* salt, and a few reactions of the acid are described.

The acids from the second fraction appear to consist of glycollic acid and the above thio-acid.　　　　　　　　　　　　　A. G. B.

Derivatives of Ethylic Cyanacetate and Ethylic Cyanosuccinate. By L. BARTHE (*Compt. rend.*, **118**, 1268—1271).— Ethylic β-bromopropionate is obtained by saturating cooled acraldehyde with gaseous hydrogen bromide, oxidising the bromaldehyde, and converting the acid into the ethylic salt.

When ethylic sodiocyanacetate is heated for some time with ethylic β-bromopropionate in presence of ethylic alcohol, *ethylic cyanoglutarate*, $COOEt\cdot CH_2\cdot CH_2\cdot CH(CN)\cdot COOEt$, is formed ; it boils at 198° under a pressure of 50 mm.

Ethylic dimethylcyanosuccinate, $COOEt\cdot CMe_2\cdot CH(CN)\cdot COOEt$, is a colourless, oily liquid, boiling at 186·5°. It is readily obtained in considerable quantity by the action of ethylic bromisobutyrate on ethylic sodiocyanacetate in presence of absolute alcohol. When boiled with methylic iodide, no action takes place.

No condensation takes place when ethylic bromiosuccinate is boiled with ethylic sodiocyanosuccinate, or heated with it in sealed tubes at 125°.

When ethylic β-cyanotricarballylate in alcoholic solution is heated for some time at 110—120° with dilute hydrochloric acid, it yields ammonium chloride, and tricarballylic acid. *Methylic tricarballylate* is obtained by mixing a solution of methylic cyanotricarballylate in methylic alcohol with a quantity of the same alcohol saturated with hydrogen chloride, and allowing the mixture to remain in a cool place for many months. It is a colourless, oily liquid, soluble in alcohol, but insoluble in alkalis ; it boils at 228° under a pressure of 45 mm.　　　　　　　　　　　　　　　C. H. B.

Ricinoleic acid, Ricinelaïdic acid, and Ricinostearolic acid. By C. MANGOLD (*Monatsh.*, **15**, 307—315).—Ricinoleic acid distils under 50 mm. pressure at 250°, leaving a dark viscid residue in the retort. The distillate, which has the composition $C_{18}H_{32}O_2$, is a colourless oil at ordinary temperatures, but solidifies in a freezing mixture ; it gives a barium salt which is insoluble in alcohol.

Ricinelaïdic acid is obtained by treating castor oil with sodium hydroxide and pouring the mixture into warm dilute hydrochloric acid. The product is then washed with water and treated with dilute nitric acid and potassium nitrite. It crystallises from light petroleum in white crystals, and melts at 51° ; when distilled under 15—30 mm. pressure, it boils at 240—250°, but at the same time decomposes, being converted into a *new acid* of the composition $C_{18}H_{32}O_2$. This crystallises is lustrous, white tablets, and melts at 53—54°. The *ammonium salt* crystallises in lustrous leaflets and is sparingly soluble in cold water. The *tetrabromo-compound*,

$$C_{18}H_{34}Br_4O_2,$$
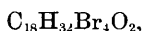
crystallises in white nodules and melts at 80—81°.

Ricinelaïdic acid, when reduced with red phosphorus and iodine, and then with zinc and hydrochloric acid, is converted into stearic acid.

Ricinelaidic hydrazide, $OH \cdot C_{17}H_{32} \cdot CO \cdot NH \cdot NHPh$, is obtained by heating the acid with phenylhydrazine at 120°. It crystallises in tufts of slender white needles, and melts at 110—110·5°.

Ricinostearolic acid, $C_{18}H_{32}O_3$, is obtained by brominating pure castor oil and boiling the product with alcoholic potash; it melts at 51°. The *barium* salt crystallises from alcohol in beautiful silky leaflets. When the acid is treated with concentrated sulphuric acid, it is converted into hydroxystearoricinic acid. This separates in white crystals and melts at 78—80°. E. C. R.

Derivatives of Glycollic Acid. By C. A. BISCHOFF and P. WALDEN (*Annalen*, **279**, 45—70).—The compound melting at 220°, and hitherto known as glycollide, is in reality a polymeride; it is best obtained by Norton and Tscherniak's method (*Bull. Soc. Chim.*, **30**, 102), namely by heating sodium chloracetate at 150°, preferably with petroleum (b. p. 150—200°). When distilled under diminished pressure, it is converted into *glycollide*, which crystallises in large plates, melts at 86—87°, and is shown by the cryoscopic method to have the formula $CH_2 {<}^{CO \cdot O}_{O \cdot CO} {>} CH_2$. Attempts to prepare glycollide by direct distillation of sodium chloracetate under diminished pressure did not yield favourable results. Glycollide may also be obtained by distilling sodium bromacetate or glycollic acid under diminished pressure (compare Abstr., 1893, i, 250; Anschütz, *ibid.*, 306). Glycollide dissolves in hot water with partial conversion into the polymeric compound, but when the aqueous solution is boiled for several hours, glycollic acid is formed.

Glycollic anilide, $OH \cdot CH_2 \cdot CO \cdot NHPh$, is obtained by boiling glycollide, polyglycollide, or glycollic acid with aniline; it crystallises in prisms (see *Zeit. Kryst. Min.*, **21**, 104) and melts at 97°. The authors failed to obtain the acicular modification (m. p. 108°) described by Norton and Tscherniak (*Ber.*, **12**, 285). *αγ-Dichloro-β-anilacetoacetanilide chloride*, $CH_2Cl \cdot C(NPh) \cdot CHCl \cdot CCl{:}NPh$, is obtained by treating glycollic anilide with phosphorus pentachloride; it crystallises from acetone in yellow needles, commences to decompose at 209°, and is identical with the compound obtained by Wallach from chloracetanilide and phosphorus pentachloride (*Annalen*, **184**, 97). If treated with alcoholic soda, a *base*, $NPh{:}C {<}^{CHCl}_{CHCl} {>} C{:}NPh$, is obtained, which crystallises in almost colourless needles, and melts at 133—134°; this, by treatment with concentrated hydrochloric acid, is reconverted into the original substance. The latter, when reduced with zinc dust and acetic acid, gives a compound,

$$CH_2Cl \cdot C(NPh) \cdot CH_2 \cdot CH{:}NPh,$$
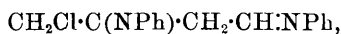
melting at 172°, and when reduced in alkaline solution a non-chlorinated derivative is formed.

Dichloracetanilide, $CHCl_2 \cdot CO \cdot NHPh$, (m. p. 116—117°) is obtained by treating chloracetanilide with phosphorus pentachloride; chloracetanilide, $CH_2Cl \cdot CONHPh$, is produced when glycollic anilide is dissolved in phosphorus oxychloride and the solution is treated with

phosphorus pentachloride, the liquid portion distilled under di-
minished pressure, and the residue extracted with hot water. *Phos-
phoric triglycollic anilide*, $PO(O \cdot CH_2 \cdot CO \cdot NHPh)_3$, is formed by treat-
ing glycollic anilide in a variety of ways with phosphorus penta-
chloride or phosphorus oxychloride; this compound is precipitated
on adding water to the product, which must not be distilled. It
forms colourless needles, melts at 196°, and dissolves in hot soda under-
going partial decomposition. The ultimate product of the action of
phosphorus pentachloride (5 mols.) on glycollic anilide is oxanilide.

Glycollic orthotoluidide, $OH \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_4Me$, is prepared from
polyglycollide, or glycollic acid, and orthotoluidine; it crystallises in
long needles and melts at 67°. The compound (m. p. 188—189°)
previously described as glycolic orthotoluidide (Abstr., 1890, 1161)
is probably diacetylglycolylethylenediorthotolyldiamine

$$C_2H_4[N(C_6H_4Me) \cdot CO \cdot CH_2 \cdot OAc]_2.$$
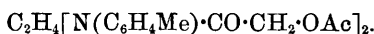
Phosphoric diglycollic orthotoluidide,

$$OH \cdot PO(O \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_4Me)_2,$$
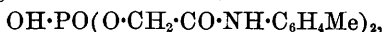
is formed by shaking glycollic orthotoluidide dissolved in dry chloro-
form with the calculated quantity of phosphorus pentachloride; it
melts at 168—170°. *Phosphoric triglycollic orthotoluidide*,

$$PO(O \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_4Me)_3,$$

is formed, on allowing the last-mentioned reagents to remain together
for 12 hours; it melts at 143°. *Chloracetylorthotoluidide*,

$$CH_2Cl \cdot CO \cdot NH \cdot C_6H_4Me,$$

is obtained by treating with water the chloroform filtrate from the
last-described compound; it melts at 111—112°, and has been de-
scribed by Abenius and Widman (*J. pr. Chem.*, [2], **38**, 299).

Glycollic paratoluidide, $OH \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_4Me$, melts at 143°.
When treated with phosphorus pentachloride *αγ-dichloro-β-paratolyl-
acetoaceticparatoluidoimidochloride*,

$$CH_2Cl \cdot C(N \cdot C_6H_4Me) \cdot CHCl \cdot CCl \cdot N \cdot C_6H_4Me)$$
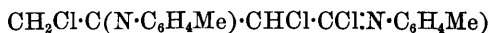
is formed; it sinters at 270°, and is converted into the *compound*,

$$C_6H_4Me \cdot N \cdot C \left< {CHCl \atop CHCl} \right> C \cdot N \cdot C_6H_4Me,$$

when heated with alcoholic soda; this melts at 133°.

Phosphoric triglycollic paratoluidide, $PO(O \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_4Me)_3$,
melts at 188°; *chloracetylparatoluidide* (P. Meyer, *Ber.*, **8**, 1154) melts
at 161—162°. Oxalic paratoluidide (m. p. 263°) is the ultimate product
of the action of phosphorus pentachloride on glycollic paratoluidide.
Other compounds which were not properly identified are also obtained
by the action of phosphorus pentachloride on glycollic paratoluidide.

Glycollic α-naphthalide, $OH \cdot CH_2 \cdot CO \cdot NH \cdot C_{10}H_7$, melts at 128°, and
gives acet-α-naphthalide (m. p. 159°) when heated with acetic acid.

Glycollic β-naphthalide, $OH \cdot CH_2 \cdot CO \cdot NH \cdot C_{10}H_7$, melts at 138° and
yields aceto-β-naphthalide (m. p. 132°) when heated with acetic
anhydride.

Phosphoric triglycollic β-naphthalide $PO(O \cdot CH_2 \cdot CO \cdot NH \cdot C_{16}H_7)_3$, melts at 192—196°.
<div align="right">A. R. L.</div>

Derivatives of Lactic acid. By C. A. BISCHOFF and P. WALDEN (*Annalen*, **279**, 71—99).—Lactide, $CHMe{<}^{CO \cdot O}_{O \cdot CO}{>}CHMe$, contains two asymmetrical carbon atoms in its molecule, and should, therefore, exist in other modifications. The authors have prepared lactide by heating ordinary inactive lactic acid or sodium α-bromopropionate (see Abstr., 1893, i, 250), but found that with the exception of oily bye-products, the ordinary lactide (m. p. 124·5°) alone was obtained; unlike glycollide (last abstract), it does not polymerise. When heated with aniline, lactanilide (Leipen, Abstr., 1888, 580) is formed; the latter yields acetanilide when heated with acetic anhydride, and, if treated with phosphorus pentachloride, the *compound*,

$$OH \cdot CMeCl \cdot CCl(ONH_3Ph) \cdot NHPh,$$
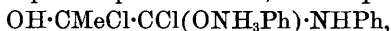
is obtained, which melts at 79—82°, and decomposes into pyruvic anilide when dissolved in hot water.

Pyruvic anilide is also obtained directly from lactanilide when it is warmed with phosphorus pentachloride; in addition to the properties described by Nef (Abstr., 1892, 1440; compare also Abstr., 1893, i, 511), it is observed that the compound decomposes at 252°.

α-Chloropropanilide, $CHMeCl \cdot CO \cdot NHPh$, is obtained by treating a solution of lactanilide in benzene with phosphorus pentachloride. It forms colourless plates, and melts at 92°.

Phosphoric trilactanilide, $PO(O \cdot CHMe \cdot CO \cdot NHPh)_3$, is one of the products obtained when lactanilide is heated with phosphorus pentachloride, but it is best prepared by the action of phosphorus pentachloride on a solution of the anilide in phosphorus oxychloride; it melts at 205°.

Lactic orthotoluidide melts at 75—76° (compare Leipen, *loc. cit.*), and yields pyruvic orthotoluidine when warmed with phosphorus pentachloride; this dissolves in aqueous sodium hydroxide, and on acidifying the solution, a *polymeride*, $C_{20}H_{22}N_2O_4$, melting at 177°, separates. The *compound* (m. p. 111°) formerly regarded as a hydrated orthotoluidide (Abstr., 1893, i, 511) is in reality a chlorinated compound, $C_{10}H_{12}NClO$; it is formed by boiling lactanilide with benzene and phosphorus pentachloride.

Phosphoric trilactic orthotoluidide, $PO(O \cdot CHMe \cdot CO \cdot NH \cdot C_6H_4Me)_3$, melts at 177°.

Lactic paratoluidide melts at 107° (compare Leipen, *loc. cit.*); if treated with phosphorus pentachloride, it is converted into *pyruvic paratoluidide*, $C_{10}H_{11}NO_2$, which melts at 109°. When a solution of the latter in alkalis is acidified, a *polymeric compound*, $C_{20}H_{22}N_2O_4$, melting at 207°, is obtained.

Phosphoric trilactic paratoluidide, $PO(OCHMe \cdot CO \cdot NH \cdot C_6H_4Me)_3$, melts at 156°.

When lactic paratoluidide is heated with phosphorus pentachloride, the product distilled in a vacuum, and the residue fractionally crystallised from alcohol, α-chloropropionic paratoluidide,

$$CHMeCl \cdot CO \cdot NH \cdot C_6H_4Me,$$

melting at 124°, and *α-dichloropropionic paratoluidide*,

$$CMeCl_2 \cdot CO \cdot NH \cdot C_6H_4Me,$$

melting at 84—86°, are obtained.

Lactic methylanilide, $OH \cdot CHMe \cdot CO \cdot NMePh$, prepared by heating lactide or lactic acid with methylaniline, melts at 95—96°; when treated with phosphorus pentachloride, it yields a mixture consisting principally of oily substances.

Glyceric paratoluidide, $OH \cdot CH_2 \cdot CH(OH) \cdot CO \cdot NH \cdot C_6H_4Me$, melts at 120—122°, and differs from the analogous compounds, containing but one hydroxyl group in that it dissolves in cold alkalis.

Lactic α-naphthalide, $OH \cdot CHMe \cdot CO \cdot NH \cdot C_{10}H_7$, melts at 108°, and decomposes into its proximate constituents when heated with acetic anhydride; the benzoyl derivative melts at 155°. By the action of phosphorus pentachloride on the α-naphthalide, there are obtained— *pyruvic α-naphthalide*, $COMe \cdot CO \cdot NH \cdot C_{10}H_7$, which melts at 102—103°, and yields a *polymeride* melting at 202—203°; and *phosphoric trilactic α-naphthalide*, $PO(O \cdot CHMe \cdot CO \cdot NH \cdot C_{10}H_7)_3$, melting at 166—169°.

Lactic β-naphthalide, $OH \cdot CHMe \cdot CO \cdot NH \cdot C_{10}H_7$, melts at 137·5°, and behaves with acetic anhydride in a manner analogous to the α-derivative; the *benzoyl* derivative melts at 177°. A. R. L.

Derivatives of the two α-Hydroxybutyric acids. By C. A. BISCHOFF and P. WALDEN (*Annalen*, **279**, 100—118).—α-Hydroxybutyric acid is best prepared by heating α-bromobutyric acid with a solution of potassium carbonate (1 mol.). It boils at 140° under a pressure of 14 mm., and the chief portion distils at 225° under a pressure of 764 mm., being meanwhile converted into the lactide, so that the whole does not pass over until a temperature of 260° is attained (see also Markovnikoff, *Annalen*, **119**, 115; **120**, 279; **153**, 242). The lactide has already been described (Abstr., 1893, i, 251). The following derivatives are obtained by heating the acid or the lactide with the corresponding bases at 180°. The *anilide*,

$$CH_2Me \cdot CH(OH) \cdot CO \cdot NHPh,$$

melts at 90°; the *orthotoluidide* at 57°; and the *paratoluidide* at 112—113°. When the latter is treated with phosphorus pentachloride in chloroform solution, it yields *propionylformoparatoluidide*, $CH_2Me \cdot CO \cdot CO \cdot NH \cdot C_6H_4Me$, which forms monoclinic crystals, and melts at 130—131°; if dissolved in alkali and reprecipitated with acid, a polymeride melting at 192°, probably $C_{22}H_{26}N_2O_4$, is obtained. The yield of the *α-naphthalide*, which melts at 96°, is small; whilst by heating α-hydroxybutyric acid with β-naphthylamine, *ββ-di-naphthylamine* (Abstr., 1892, 1337) is produced, together with a small amount of the *β-naphthalide* melting at 126°.

Sodium α-bromisobutyrate, $C_4H_6BrO_2Na + \frac{1}{2}H_2O$, crystallises in colourless, microscopic needles; its behaviour on distillation is described (Abstr., 1893, i, 251). When α-hydroxyisobutyric acid is treated with phosphorus pentachloride and the product distilled, carbonic anhydride is evolved, and aldehyde, acetone, acetic acid, and an unknown compound having the odour of camphor and boiling

at 150—155°, pass over. Neither by the method just described, nor by heating α-hydroxyisobutyric acid at 200—215°, was it found possible to prepare the lactide.

α-*Hydroxyisobutanilide*, $OH \cdot CMe_2 \cdot CO \cdot NHPh$, forms colourless, rhombic tables, and melts at 136°. When treated with phosphorus pentachloride, it yields a *hydrochloride*, $OH \cdot CMe_2 \cdot CO \cdot NHPh, HCl$, melting at 113°, and decomposing into the anilide when boiled with water; besides this, α-*chlorisobutanilide*, $CMe_2Cl \cdot CO \cdot NHPh$, melting at 67—68°, is also formed. If α-hydroxyisobutanilide is dissolved in chloroform containing phosphorus oxychloride, and the solution treated with phosphorus pentachloride, an unstable *compound* is obtained which melts at 113°, and, when boiled with water or alcohol, decomposes yielding *phosphoric trihydroxyisobutanilide*,

$$PO(O \cdot CMe_2 \cdot CO \cdot NHPh)_3,$$

melting at 158—159°.

α-*Hydroxyisobutyric orthotoluidide*, $OH \cdot CMe_2 \cdot CO \cdot NH \cdot C_6H_4Me$, melts at 88°, and, when treated with phosphorus pentachloride, yields *phosphoric trihydroxyisobutyric orthotoluidide*,

$$PO(O \cdot CMe_2 \cdot CO \cdot NH \cdot C_6H_4Me)_3,$$
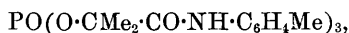
melting at 194—196°, and α-*chlorisobutyric orthotoluidide*,

$$CMe_2Cl \cdot CO \cdot NH \cdot C_6H_4Me,$$

melting at 56—59°.

α-Hydroxyisobutyric paratoluidide has been already described by Tigerstedt (Abstr., 1893, i, 53). *Phosphoric trihydroxyisobutyric paratoluidide* melts at 160—162°, and α-chlorisobutyric paratoluidide at 70°.

α-*Hydroxyisobutyric naphthalide* melts at 159—161°.

By the action of α-hydroxyisobutyric acid on β-naphthylamine, $\beta\beta$-dinaphthylamine is not formed as in the case of α-hydroxybutyric acid, but α-*hydroxyisobutyric* β-*naphthalide* (Tigerstedt, *loc. cit.*) is obtained. A. R. L.

Isosuccinic acid and Isomalic acid. By M. PUSCH (*Arch. Pharm.*, **232**, 186—221).—The author finds that, contrary to the statements of Krestownikoff (this Journal, 1877, ii, 442), isosuccinic acid is the product of the reaction between ethylic α-bromopropionate and potassium cyanide, whether in alcoholic or aqueous solution. Isosuccinic acid melts at 134°, and is soluble in 1·1 parts of water at 17°; the solutions of its normal and acid alkali salts are precipitated by calcium chloride and barium chloride even when the dilution is 1 : 50, particularly on heating.

Ammonium ($1H_2O$) and *copper* ($3H_2O$) *isosuccinates* are described as being novel salts (compare Beilstein, [3], **1**, 663), and the known salts have been prepared, the amount of water of crystallisation being in some cases corrected.

The author confirms the statements of Schmöger and of Brunner (Abstr., 1893, i, 145) as to the properties of isomalic acid. He has

also prepared Böttinger's "methyltartronic acid" (*Ber.*, **14**, 148), but finds that the product has the formula $C_5H_6O_5$, and is possibly hydroxycitraconic acid. The presence of a molecule of water of crystallisation appears to have misled Böttinger.   A. G. B.

Derivatives of Glutamic acid. Pyroglutamic acids and Pyroglutamides. By A. MENOZZI and G. APPIANI (*Gazzetta*, **24**, i, 370—391; compare Abstr., 1892, 298).—Haitinger (*Monatsh.*, **3**, 228) prepared inactive pyroglutamic acid by heating dextroglutamic acid at 180—190°; the authors find, however, that on heating dextroglutamic acid at 150—160°, water is evolved and *lævopyroglutamic acid*,

$$\begin{matrix} COOH \cdot CH \cdot NH \\ | \qquad\qquad \\ CH_2 \cdot CH_2 \end{matrix} >CO,$$

is formed. It is obtained in large, colourless, orthorhombic crystals melting at 162°;

$$a : b : c = 1\cdot5034 : 1 : 1\cdot6292.$$

In a 12·8 per cent. aqueous solution at 17°, it has the specific rotatory power $[\alpha]_D = -7\cdot21°$, and is more soluble in water than the inactive modification into which it is converted by heating at 180°. On boiling with barium hydroxide, it yields dextroglutamic acid.

Silver dextroglutamate, $C_5H_7NO_4Ag_2$, and *silver hydrogen dextroglutamate*, $C_5H_8NO_4Ag$, are white, insoluble powders.

The substance, which the authors have previously described as inactive glutimide, seems to have the constitution

$$\begin{matrix} NH_2 \cdot CO \cdot CH \cdot NH \\ | \qquad\qquad\quad \\ CH_2 \cdot CH_2 \end{matrix} >CO;$$
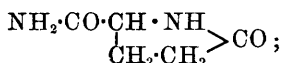
it is lævorotatory, the specific rotation for the anhydrous substance being $[\alpha]_D = -40°$. When heated with alcoholic ammonia at 140—150°, or alone at 200°, it yields inactive pyroglutamide (Haitinger's glutimide); on boiling with caustic alkalis, it is converted into dextroglutamic acid. It yields a *hydrochloride*,

$$C_5H_8N_2O_2,HCl,$$

which crystallises in needles in the cold, but when boiled with hydrochloric acid, it gives dextroglutamic acid hydrochloride.

The authors have previously shown that on crystallising inactive glutamic acid from water, right- and left-handed enantiomorphous crystals are deposited; this fact could not be conveniently utilised for the preparation of the unknown lævoglutamic acid, neither could the latter substance be prepared by crystallising the racemic modification with alkaloïds. By cultivating *Penicillium glaucum* in solutions of the mixture, however, the dextro-acid was destroyed, and *lævoglutamic acid* was left in solution. The lævo-acid is in all respects similar to the dextro-acid, but the rotation is to the left, $[\alpha]_D = -12\cdot9°$, and the crystals possess the left-handed enantiomorphous form. It is of interest to note that whilst the dextro-acid has a characteristic taste, the lævo-isomeride is almost tasteless.

Dextropyroglutamide is obtained by heating a solution of lævoglutamic acid in absolute alcohol saturated with hydrogen chloride,

and treating the ethylic salt with alcoholic ammonia; in a 3·3 per cent. aqueous solution, it has the specific rotation $[\alpha]_D = +41·29°$, and has the same melting point and other properties as its lævo-isomeride. On boiling it with barium hydroxide, *dextropyroglutamic acid* is obtained; this has the specific rotation $[\alpha]_D = +7°$ in a 2·6 per cent. aqueous solution, and is in all other respects similar to its lævo-isomeride.

In addition to the methods already given by the authors, inactive glutamic acid may be prepared by the following processes: by heating dextroglutamic acid at 160—170° with barium hydroxide, and by heating inactive pyroglutamide with barium hydroxide or hydrochloric acid. The *ethylic* salt resembles its dextro-isomeride in appearance, but melts at 185°. On heating the acid at 150—160°, it is converted into inactive pyroglutamide; this substance, which may be prepared by a variety of methods, crystallises anhydrous, and melts at 214°. It yields a crystalline *hydrochloride*, and, on boiling with hydrochloric acid, gives inactive glutamic acid hydrochloride.

Inactive silver pyroglutamate, $C_5H_6NO_2Ag$, is obtained as a white, crystalline mass. On heating the free acid with barium hydroxide, inactive glutamic acid is obtained, whilst if treated with alcoholic ammonia, it yields inactive pyroglutamide; on passing hydrogen chloride into its alcoholic solution, inactive ethylic glutamate is obtained.   W. J. P.

Suberic, Azelaïc, and Sebacic Anhydrides. By F. ANDERLINI (*Gazzetta*, **24**, i, 474—477).—*Suberic anhydride,* $C_6H_{12}{<}^{CO}_{CO}{>}O$, is prepared by boiling suberic acid with acetic chloride; it is obtained as a crystalline, white powder melting at 62—63°, and is very soluble in benzene.

Azelaïc anhydride, $C_7H_{14}{<}^{CO}_{CO}{>}O$, prepared from azelaïc acid in the same manner, closely resembles the preceding anhydride, and melts at 52—53°. This process also affords a ready means of preparing sebacic anhydride.   W. J. P.

Emetics. By P. ADAM (*Compt. rend.*, **118**, 1273—1275).—It is generally assumed that in the emetics the antimonious hydroxide, ferric hydroxide, or boric anhydride has a basic function, but Jungfleisch has advanced evidence to show that they really have an acid function. It is noteworthy that only acids which have a phenolic or alcoholic function form compounds with antimonious oxide, &c. Oxalic acid and phthalic acid, and their salts, do not combine with boric anhydride. In the preparation of the emetics, it is a salt of the acid that must be boiled with the antimony oxide or other oxides; as a rule, the free acid yields no such product. This is well seen in the case of boric anhydride, and mucic, saccharic, and salicylic acids, and their salts. The author has also obtained compounds of sodium lactate with boric anhydride, antimonious oxide, or arsenious oxide; of potassium malate with boric anhydride or antimonious oxide; of sodium potassium tartrate with 1 or 2 mols. of boric anhydride.

Further, lactic, malic, and tartaric acids prevent the precipitation of iron by alkali hydroxides, whereas this property is shown by none of the emetics, except the monoborotartrate,

$$COOK \cdot CH(OH) \cdot CH(BO_2) \cdot COONa,$$
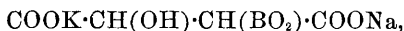
which is the only one of these compounds which contains a hydroxyl group. With sodium potassium tartrate, arsenious oxide yields the same compound as with hydrogen potassium tartrate. Potassium hydrogen tartrate combines with 1 mol. only of boric anhydride, and the resulting compound prevents the precipitation of iron by alkali hydroxides.

Tartar emetic yields no precipitate with alkalis in the cold, unless the quantity of alkali added is equivalent to that already present in the salt. Litmus indicates neutrality when only one quarter of the alkali has been added, but phenolphthaleïn, cochineal, and turmeric indicate neutrality with the theoretical quantity of alkali. On the other hand, an imperfectly neutralised solution of tartar emetic deposits antimony oxide after some time. A freshly made solution, which is acid to litmus, becomes alkaline on dilution. When potassium carbonate is added to a solution of tartar emetic, there is immediate development of heat, but not immediate formation of a precipitate, and if a quantity of hydrochloric acid equivalent to the alkali is added, the solution still shows all the properties of tartar emetic. The decomposition of the emetic by alkalis proceeds slowly, like saponification.

The author concludes that the analogies and chemical behaviour of the emetics indicate that they are ethereal salts, and not double salts, the antimony and other oxides playing the part of acids.

C. H. B.

Emetics. By E. MAUMENÉ (*Compt. rend.*, **118**, 1415—1418).—The author quotes analyses of tartar emetic and its analogues, with a view to show that the numbers obtained agree with the fractional formulæ deduced from his general law, and not with the usual simpler formulæ, in which the numbers of the atoms of the constituent elements are represented by simple whole numbers.

C. H. B.

Action of Nitrous acid on Trimethylenediamine. By N. DEMYANOFF (*J. Russ. Chem. Soc.*, **25**, 677—679).—When the nitrite of trimethylenediamine is heated in aqueous solution on the oil-bath (see next abstract), and the gases evolved are passed through bromine, a bromide is obtained which corresponds with the hydrocarbon, C_3H_4. The aqueous distillate contains allylic alcohol, and the residue a mixture of glycols, which boil chiefly at 200—210°. A glycol was isolated, the bromide of which had the composition $C_3H_6Br_2$.

J. W.

Action of Nitrous acid on Pentamethylenediamine. By DEMYANOFF (*J. Russ. Chem. Soc.*, **25**, 665—677).—The hydrochloride of pentamethylenediamine was converted into the nitrite by means of

silver nitrite, and a 10 per cent. solution of the salt thus obtained was heated in an oil-bath until decomposition occurred. The gaseous products, on being passed through bromine, gave a bromide of the composition $C_5H_9Br_4$; this crystallises from alcohol in hexagonal plates, and melts at 86—87°.

From the water which distilled over, a red, oily layer separated on adding potassium carbonate, and this, on fractionation, yielded a glycol oxide, $C_5H_{10}O$, distilling between 82° and 87°, and a primary unsaturated alcohol of the same composition, which distilled between 133° and 136°, and had the sp. gr. 0·8533 at 18·5°/0°. The acetate boils at 145—146°, and has the sp. gr. 0·8137 at 19°/0°.

From the non-volatile residue, a mixture of glycols was obtained, boiling chiefly between 228° and 238°. The author succeeded in isolating from these pentamethylene glycol, by fractionation under reduced pressure. The corresponding bromide was found to boil at 208—214°, and had the sp. gr. 1·7017 at 16·5°/0°.　　J. W.

Action of Acetic Anhydride on Succinic acid in Presence of Calcium Chloride. By G. MAGNANINI and T. BENTIVOGLIO (*Gazzetta*, **24**, i, 433—437; compare Magnanini, Abstr., 1893, i, 623).—2 : 5 : 3-*Dimethylacetylfurfuran*, $\begin{smallmatrix}C\,Ac\vdots CMe\\CH\vdots CMe\end{smallmatrix}>O$, is obtained by heating a mixture of succinic acid, acetic anhydride, anhydrous sodium acetate, and zinc chloride for eight hours, in an autoclave at 200—205°. After distilling off the acetic anhydride and acetic acid, the residue is distilled in a current of steam, when the furfuran is obtained as a volatile oil, boiling at 193—196° under 760 mm. pressure. A small quantity of another oil is formed during the process. Dimethylacetylfurfuran readily absorbs bromine, and when heated with ammonia in a closed tube at 110—115°, yields 2 : 5 : 3-dimethylacetylpyrroline.

The *oxime*, $C_8H_{11}NO_2$, is prepared by heating dimethylacetylfurfuran with hydroxylamine hydrochloride, sodium carbonate, and dilute alcohol at 150°. in a closed tube. It crystallises in silvery scales, and melts at 78°.　　W. J. P.

The Benzene Nucleus. By W. VAUBEL (*J. pr. Chem.*, [2], **50**, 58—60).—The author reconciles his formula for benzene (this vol., i, 326) with that of Kekulé. Baeyer's formula for limonene, which represents it as a $\Delta^{1,3}$-dipentene (this vol., i, 252), is open to the objection that the optical activity of limonene is not accounted for by an asymmetrical carbon atom; the author gives a figure showing that a formula for limonene, constructed on the plan of his formula for benzene, does exhibit an asymmetrical carbon atom.　　A. G. B.

Action of the Electric Current on Benzene. By L. GATTERMANN and F. FRIEDRICHS (*Ber.*, **27**, 1942—1943).—Renard (Abstr., 1880, 802) has stated that an isobenzoglycol (m. p. 171°) is obtained by the action of an electric current on benzene, dissolved in alcohol containing dilute sulphuric acid. The authors have repeated the

experiments, and find that the compound produced is quinol (m. p. 169—170°).   E. C. R.

Condensation of Dichloracetal with Benzene and Toluene.
By W. P. BUTTENBERG (*Annalen*, **279**, 324—337 ; compare this vol., i, 520).—Diphenyldichlorethane, $CHPh_2 \cdot CHCl_2$, is obtained by the condensation of dichloracetal with benzene in the presence of sulphuric acid. It crystallises from hot alcohol in colourless prisms, melts at 80°, and distils and partially decomposes at 295—305°. Faming nitric acid converts it into *dinitrodiphenyldichlorethane*, which crystallises from acetic acid in yellowish needles melting at 177—178°. Diphenyldichlorethane is converted by boiling alcoholic potash into *diphenylchlorethylene*, $CPh_2 \cdot CHCl$, which crystallises from alcohol in long needles, melting at 42°, readily soluble in ether, &c.; it boils without decomposition at 298°. When heated with water at 200°, it is not converted into the corresponding aldehyde; on distillation with lime, it yields stilbene and other products. Faming nitric acid converts it into a ketonic substance, which could not be obtained crystalline, but yielded a hydrazone; the latter melts at 234°, and has the composition of *dinitrobenzophenone hydrazone*, $C_{19}H_{14}N_4O_4$.

When diphenylchlorethylene is heated with alcoholic sodium ethoxide, it yields *diphenylvinyl ethyl ether*, $CPh_2 \cdot CH(OEt)$, along with a little tolane. The former of these is a colourless, refractive liquid, boiling at 178—182° under a pressure of 18 mm. When diphenylvinyl ethyl ether is mixed with alcohol and treated with sulphuric acid, a hydrocarbon of the composition $C_{14}H_{10}$ is obtained, which separates from light petroleum in yellowish crystals melting at 157—158°. This substance does not yield a bromine additive compound, and was not further investigated.

Diphenylvinyl ethyl ether is readily converted by acids into diphenylacetaldehyde, the preparation of this substance being best carried out by saturating with hydrogen chloride a mixture of the diphenylvinyl ether with four times its volume of glacial acetic acid, and allowing it to stand. Diphenylacetaldehyde readily condenses with phenols to form products, which may be prepared by mixing the phenol with the diphenylvinyl ether and an acetic acid solution of hydrogen chloride. *Dihydroxytetraphenylethane*, $CHPh_2 \cdot CH(C_6H_4 \cdot OH)_2$, is a red powder which melts at 230—232°. The *diacetate* crystallises in small needles and melts at 155°. *Dithymoldiphenylethane*, $CHPh_2 \cdot CH(C_{10}H_{12} \cdot OH)_2$, separates from acetic acid in colourless crystals melting at 224°. The *diacetate* forms needles melting at 152°. β-Naphthol does not behave in the normal way with diphenylacetaldehyde, but yields a substance of the formula $C_{24}H_{18}O$, which crystallises from alcohol in needles melting at 141—142°, has a molecular weight corresponding with the above formula, and does not give an acetate when heated with acetic chloride. It is possibly β-naphtho-diphenyldihydrofurfuran, $C_{10}H_6 < \!\! \begin{smallmatrix} CH_2 \\ O \end{smallmatrix} \!\! > CPh_2$.

Ditolyldichlorethane, $CHCl_2 \cdot CH(C_6H_4Me)_2$, is prepared in a manner similar to the diphenyl derivative; it is readily soluble in most solvents, crystallises in plates, and melts at 80°.

Ditolylchlorethylene, $CHCl{:}C(C_6H_4Me)_2$, forms colourless needles melting at 67°. This compound is converted by sodium ethoxide into dimethyltolane, $C_6H_4Me{\cdot}C{:}C{\cdot}C_6H_4Me$, the *tetrachloride* of which forms asymmetric crystals and melts at 183°.

Dimethyltolane can readily be converted into deoxytoluoïn, identical with that obtained by Stierlin (*Ber.*, **22**, 383) from paramethylbenz-aldehyde. The *oxime* of this substance crystallises in plates, and melts at 128°. When deoxytoluoïn is treated in alcoholic solution with sodium amalgam, the product consists of *ditolylhydroxyethane*, $C_6H_4Me{\cdot}CH_2{\cdot}CH(OH){\cdot}C_6H_4Me$, and the corresponding *pinacone*, $C_{32}H_{34}O_2$; the latter melts at 226°. Ditolylhydroxymethane, when warmed in acetic acid solution with a few drops of sulphuric acid, is converted, with loss of water, into paradimethylstilbene, $C_6H_4Me{\cdot}CH{:}CH{\cdot}C_6H_4Me$. A. H.

Iodosopseudocumene and Iodoxypseudocumene. By C. WILLGERODT (*Ber.*, **27**, 1903—1905).—*Pseudocumylic iodochloride*, $C_6H_2Me_3{\cdot}ICl_2$ ($Me_3 : ICl_2 = 1 : 2 : 4 : 5$), is obtained by passing chlorine into a well-cooled solution of iodopseudocumene in chloroform or acetic acid, the latter giving the purest product. It separates from acetic acid in prisms which melt and decompose at 67—68°, and froth up rapidly at 70°. When treated with potassium or sodium carbonate, the iodochloride is converted into *iodosopseudocumene*, $C_6H_2Me_3{\cdot}IO$, which, after removal of iodopseudocumene with chloroform, remains as a jelly, and on drying forms a pale yellow, amorphous powder. It is soluble to some extent in acetic acid, but could not be obtained crystalline. When heated, it changes colour at 120—125°, chemical change probably taking place, and the product on further heating decomposes completely at 171—175°.

Iodoxypseudocumene, $C_6H_2Me_3{\cdot}IO_2$, is best prepared by boiling the crude iodoso-compound with water, and, on boiling off the latter, separates in plastic white needles, which decompose with explosion at 212°; it is only sparingly soluble in chloroform and alcohol, and insoluble in the other common solvents. H. G. C.

Syntheses with Sodium and Nitriles. By R. WALTHER (*J. pr. Chem.* [2], **50**, 91—92).—The author has attempted to substitute another compound which shows a tendency to undergo condensation, for the third molecule of the nitrile, in Meyer's method for effecting the condensation of nitriles by means of sodium (Abstr., 1889, 114). By the use of ethylic formate and acetate with benzonitrile, oily products have been obtained but not yet identified. With benzo-nitrile and aniline, Bernthsen's benzenylphenylamidine, melting at 114°, was obtained. Phenylhydrazine (1 mol.), benzonitrile (2 mols.), and sodium (2 mols.) yielded a *compound*, $C_{13}H_{10}N_2$, melting at 102° ; this is still under examination. A. G. B.

Electrolytic Reduction of Aromatic Nitro-compounds. By L. GATTERMANN (*Ber.*, **27**, 1927—1941).—The reduction in strong sulphuric acid solution is brought about as previously described by the author (Abstr., 1893, i, 566, and this vol., i, 72). A detailed

account of the methods employed to separate the reduction compound from the acid solution is given in the original paper.

The compound previously obtained from orthonitrotoluene is not an amidocresol, but a sulphonic acid of the same. It crystallises in colourless needles, and, when hydrolysed with hydrochloric acid, yields the amidocresol [Me : NH₂ : OH = 1 : 2 : 5]. This melts at 173°, and yields a dibenzoate melting at 160—161°.

The products of reduction of the following compounds have been examined:—Metanitrotoluene yields a sulphonic acid, and the sulphate of the amidocresol [Me : NH₂ : OH = 1 : 3 : 6]. The latter melts at 173°, and its dibenzoate at 192—193°. Nitroparaxylene yields amidoxylenol [Me : NH₂ : Me : OH = 1 : 2 : 4 : 5], which crystallises in pale yellow needles, melts and decomposes at 238°, and, when treated with ferric chloride, is quantitatively converted into paraxyloquinone (m. p. 124°).

Metabromonitrobenzene yields bromamidophenol [NH₂ : Br : OH = 1 : 3 : 4], which crystallises in colourless needles, melts and decomposes at 163°, and yields a dibenzoate melting at 192°. Bromonitrotoluene [Me : NO₂ : Br = 1 : 2 : 4] yields the *bromamidocresol* [Me : NH₂ : Br : OH = 1 : 2 : 4 : 5], which crystallises in colourless needles, melts at 215°, is converted into a bromotoluquinone melting at 106° by oxidation with ferric chloride, and yields a *dibenzoate* melting at 229°. Bromonitrotoluene [Me : NO₂ : Br = 1 : 3 : 4] yields the *bromamidocresol* [Me : NH₂ : Br : OH = 1 : 3 : 4 : 6]. This crystallises in colourless needles, melts at 180°, and yields the same bromotoluquinone as the preceding bromamidocresol. The *dibenzoate* crystallises in colourless needles and melts at 200°.

Methylic metanitrobenzoate yields *methylic amidosalicylate*
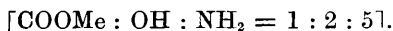
$$[\text{COOMe} : \text{OH} : \text{NH}_2 = 1 : 2 : 5].$$

This crystallises in thick needles, melts at 96°, and gives a violet-red coloration with ferric chloride. Methylic metanitroparatoluate yields the *methylic amidocresotate* [COOMe : OH : Me : NH₂ = 1 : 2 : 4 : 5], which crystallises in long, lustrous needles, and melts at 92°. The ethylic salts of the preceding acids yield similar reduction compounds. *Ethylic amidocresotate* crystallises in colourless needles and melts at 71—72°. Methylic nitrocuminate yields the *compound*

$$\text{OH·C}_6\text{H}_2\text{Pr}(\text{NH}_2)\text{·COOMe}$$
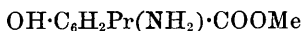
[COOMe : OH : Pr : NH₂ = 1 : 2 : 4 : 5], which crystallises in bright yellow, lustrous needles and melts at 75—76°. The corresponding *ethylic salt* crystallises in colourless leaflets and melts at 61°.

Orthonitrocinnamic acid yields *amidohydroxycinnamic acid*

$$[\text{C}_2\text{H}_2\text{COOH} : \text{NH}_2 : \text{OH} = 1 : 2 : 5];$$
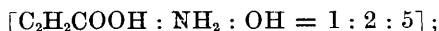
this crystallises from water with 1H₂O in broad, yellowish needles, is decomposed when heated, and when heated with concentrated hydrochloric acid at 160° is converted into hydroxycarbostyril. The *methylic salt* prepared from methylic nitrocinnamate crystallises in beautiful golden yellow needles, and melts at 178—179°.

Metanitrocinnamic acid yields an amidohydroxycinnamic acid which is immediately converted into amidocoumarin,

$$NH_2 \cdot C_6H_3 \! < \! \begin{array}{c} CH \!=\! CH \\ | \quad\quad | \\ O \!-\!\!-\! CO \end{array} .$$
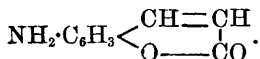
This crystallises in long bright yellow needles and melts at 168°. The *acetyl-derivative* melts at 216—217°. The *benzoyl-derivative* crystallises in colourless needles and melts at 173. Ethylic metanitrocinnamate yields the same reduction product as the free acid.

The following hydroxysulphonic acids were obtained by electrolytic reduction :—Amidohydroxybenzenesulphonic acid [$NH_2 : SO_3H : OH = 1 : 3 : 4$] separates in silvery crystals, and yields paramidophenol on hydrolysis. Amidocresolsulphonic acid [$Me : NH_2 : SO_3H : OH = 1 : 2 : 4 : 5$] crystallises in broad, lustrous needles, decomposes when heated, and yields orthoamidometacresol on hydrolysis.

Amidohydroxyquinoline [$OH : NH_2 = 1 : 4$] is obtained by the electrolytic reduction of nitroquinoline [$NO_2 = 4$]; it melts at 143°. The *dibenzoyl-compound* crystallises in colourless plates, and melts at 205°. The *diacetyl-compound* crystallises in pale yellow needles, and melts at 206—207°. The *sulphate* crystallises in long needles, and, when treated with benzaldehyde, yields the *benzylidene-derivative* $OH \cdot C_9NH_5 \cdot N \! : \! CHPh$, which crystallises from alcohol, and decomposes on heating.

Amidohydroxyquinoline [$OH : NH_2 = 4 : 1$], obtained in a similar way to the preceding, separates in colourless crystals which turn green on exposure to air; it decomposes when heated, and quickly oxidises in alkaline solution, forming a bluish-green precipitate. The *diacetyl-compound* crystallises in colourless needles, and melts at 153—154°. The *dibenzoyl-compound* crystallises in thick prisms, and melts at 180°.

Amidohydroxymethylquinoline [$NH_2 : Me : OH = 4 : 3 : 1$], obtained from nitromethylquinoline [$NO_2 : Me = 4 : 3$], crystallises in long, brownish-yellow needles, and melts at 123°. E. C. R.

Ethereal Salts and Ketones from Phenols and Halogen Substituted Fatty Acids. By S. DZIERZGOWSKI (*Ber.*, **27**, 1983—1989). —The author has recently prepared a number of condensation products by the interaction of phenols with halogen substituted acids in presence of phosphorus oxychloride. Catechol and chloracetic acid, bromacetic acid, α-chloropropionic acid, α-bromopropionic acid, and α-bromobutyric acid yield haloïd ketones ; phenol, quinol, and guaiacol, under the same conditions, yield ethereal salts ; whilst resorcinol and chloracetic acid combine to form a yellowish-red dye with a green fluorescence. A number of crystalline products are also formed from chloracetopyrogallol (this vol., i, 518) and ammonia, methylamine, dimethylamine, aniline, methylaniline, dimethylaniline, paramidomethoxybenzene, quinoline, pyridine, and piperidine respectively. Of the phenylenediamines, only the ortho-derivative reacts with chloracetocatechol and chloracetopyrogallol, forming, with the former, *anhydrophenylenediimidoglycocatechol*,

$$\begin{array}{c} CO \cdot CH_2 \cdot NH \\ | \quad\quad\quad\quad\quad > \! C_6H_4, \\ OH \cdot C_6H_3 \!-\! O \cdot NH \end{array}$$
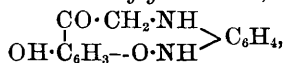
crystallising in yellow needles; it decomposes at about 245° without melting, is only sparingly soluble in alkalis, but readily in concentrated sulphuric acid, being precipitated in red needles on dilution. The *acetyl-derivative* crystallises in colourless needles, melts at 141°, and gives no coloration with ferric chloride. *Anhydrophenylene-diimidoglycopyrogallol* is prepared in a similar manner to the catechol derivative which it closely resembles; it decomposes at 290° without melting, and gives a green coloration with ferric chloride. The *diacetyl-derivative* crystallises in colourless needles, and melts at 143°.

Aniline and chloracetocatechol combine to form an *anilide*, $C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot NHPh$. The *sulphate* crystallises in colourless needles melting at 208°; when treated with nitrous acid, phenol is eliminated, and *catecholglycophenyltriazine*,

$$C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot NPh \cdot N{:}N \cdot CH_2 \cdot CO \cdot C_6H_3(OH)_2,$$
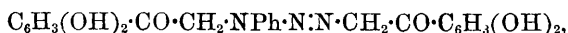
is formed; this crystallises in slender, yellow needles, melts and decomposes at 115°, is extremely unstable, and is decomposed by alkalis and by acids. *Catecholglycotolyltriazine* is prepared in a similar manner to the phenyl derivative which it closely resembles, it crystallises in prismatic needles, melts and decomposes at 120°, and is tolerably stable towards acids and alkalis. Attempts to reduce this compound were unsuccessful.

Catecholglycothiocyanate, $C_6H_3(OH)_2CO \cdot CH_2 \cdot S \cdot CN$, is prepared by the action of potassium or ammonium thiocyanate on chloracetocatechol, and crystallises from water in colourless prisms, melting at 147—150°; it gives a dark green coloration with ferric chloride, and yields a metallic mirror with alkaline silver solutions. *Pyrogallolglycothiocyanate*, formed in a similar manner to the preceding compound, crystallises in colourless needles melting at 196°.

The action of amines on ethereal chloracetates takes place in two stages, the amine radicle displaces the chlorine group, and the resulting compound is then hydrolysed by the remaining base; thus phenylic chloracetate and quinol chloracetate both yield phenyl-glycocineanilide by the action of aniline. Dimethoxyacetocatechol, $C_6H_3Ac(OMe)_2$, has also been prepared, and proves to be identical with Nietzel's "acetoveratrone" (Abstr., 1892, 61); acetopyrocatechol obtained by the reduction of chloracetocatechol with tin and hydrochloric acid is therefore identical with Neitzel's "aceto-catechone," $C_6H_3Ac(OH)_2$; it melts at 116°, not at 96—98° as stated (*loc. cit.*).   J. B. T.

Benzoresorcinol. By A. KOMAROWSKY and S. V. KOSTANECKI (*Ber.*, **27**, 1997—2000).—Dihydroxybenzophenone,

$$C_6H_3(OH)_2Bz[OH : OH : Bz = 1 : 3 : 4],$$

is prepared by the action of benzoic trichloride on resorcinol in aqueous solution, or by heating resorcinol with benzoic acid and zinc chloride at 160°. Its constitution is established both by its analogy to resacetophenone and by the production of β-phenylumbelliferone, the *acetyl-derivative* of which crystallises in silky, lustrous needles

melting at 123°. *Trihydroxybenzophenone* [OH : OH : Bz = 1 : 3 : 4; CO : OH = 1 : 4], obtained from resorcinol, parahydroxybenzoic acid, and zinc chloride, crystallises with $2H_2O$ in yellow needles, and melts at 200—201°. *Dihydroxymethoxybenzophenone* [OH : OH : Bz = 1 : 3 : 4; CO : OMe = 1 : 4] is formed from resorcinol and paramethoxybenzoic acid, and crystallises in needles melting at 165°. *Tetrahydroxybenzophenone* [OH : OH : Bz = 1 : 3 : 4; CO : OH : OH = 1 : 3 : 4], obtained from resorcinol and 3 : 4-dihydroxybenzoic acid, crystallises with $2H_2O$ in almost colourless needles, melts at 201—202°, and dyes mordanted cloth ; the colours produced resemble those given by maclurin, but are feebler.

J. B. T.

Triethylphloroglucinol. By A. COMBES (*Compt. rend.*, **118**, 1336—1339).—The author has previously shown that the action of anhydrous aluminium chloride on butyric chloride yields a solid compound, $C_{12}H_{18}O_3$, which, although it contains no hydroxyl group, behaves as a monobasic acid, and forms salts which are neutral to litmus and phenophthaleïn.

If the aluminium chloride and butyric chloride are mixed with a large quantity of chloroform instead of being allowed to act directly on one another, only 2 mols. of the acid chloride condense instead of three, and when the product is treated with water, carbonic anhydride is given off, and dipropyl ketone is formed. It follows that the first stage in the condensation is the production of the compound $CH_2Me\cdot CH_2\cdot CO\cdot CH(COCl)\cdot CH_2Me$, which is subsequently attacked by the third molecule of butyric chloride with formation of the compound $C_{12}H_{18}O_3$. If the latter is heated with excess of dilute potassium hydroxide solution in sealed tubes at 150—160° for two hours, it splits up quantitatively into dipropyl ketone, carbonic anhydride, and normal butyric acid. When heated on a water bath with phenyl hydrazine, it combines with 3 mols. of that compound.

This compound, $C_{12}H_{18}O_3$, is therefore analogous to phloroglucinol, which, according to Baeyer's researches, must be regarded as a hexamethylene derivative. The author finds that when phloroglucinol is heated with excess of dilute potassium hydroxide solution in sealed tubes at 160°, it splits up quantitatively into acetone, acetic acid, and carbonic anhydride. It follows that the compound $C_{12}H_{18}O_3$ is triethylphloroglucinol.

C. H. B.

Condensation of Dichloracetal with Anisoïl and Phenetoïl. By H. WIECHELL (*Annalen*, **279**, 337—344; compare this vol., i, 502, 520).—*Dianisyldichlorethane*, $CHCl_2\cdot CH(C_6H_4\cdot OMe)_2$, crystallises in stellate groups of prisms, melting at 113°. *Dianisylchlorethylene*, $CHCl:C(C_6H_4\cdot OMe)_2$, separates from alcohol in lamellæ, which have a bluish iridescence; it melts at 76°. *Paradimethoxytolane*, $OMe\cdot C_6H_4\cdot C:C\cdot C_6H_4\cdot OMe$, forms colourless plates melting at 142°, and sparingly soluble in ether. The *dibromide* is a sparingly soluble substance, and crystallises from acetic acid in long, slender needles melting at 197°, whilst the *tetrachloride* crystallises in cubes,

and melts at 169°. Dimethoxytolane is converted by heating with acetic and sulphuric acids into deoxyanisoïn, which melts at 108—109° (stated by Rossel, *Annalen*, **151**, 40, 42, as 95°). The *oxime* of this ketone crystallises in prisms melting at 125°. *Anisil-monoxime*, OMe·C_6H_4·C(NOH)·CO·C_6H_4·OMe, prepared from deoxy-anisoïn by Claisen's method (*Ber.*, **22**, 379), forms colourless, slender needles melting at 130°.

Dianisylhydroxyethane, OMe·C_6H_4·CH_2·CH(OH)·C_6H_4·OMe, is obtained by the reduction of deoxyanisoïn, and crystallises from alcohol in slender needles melting at 170°. Paradimethoxystilbene, OMe·C_6H_4·CH:CH·C_6H_4·OMe, is prepared by treating dianisyl-hydroxyethane with acetic and hydrochloric acids. The *dibromide* crystallises from carbon bisulphide in slender needles, melting at 145°.

Diphenetyldichlorethane, $CHCl_2$·CH(C_6H_4·OEt)$_2$, crystallises in concentrically grouped needles melting at 72°. *Diphenetylchlor-ethylene* crystallises in lustrous plates, and melts at 67°. *Para-diethoxytolane* separates from acetic acid in long, highly refractive needles melting at 162°. The *dibromide* forms flat needles melting at 210°, whilst the *tetrachloride* melts at 172. *Deoxyphenetoïn*, OEt·C_6H_4·CH_2·CO·C_6H_4·OEt, crystallises from alcohol in plates, and melts at 102°. The *oxime* separates from benzene in needles melting at 119°. *Phenetilmonoxime* crystallises from alcohol in small needles melting at 136°. *Diphenetylhydroxyethane* forms slender, white needles melting at 147°. *Paradiethoxystilbene* crystallises in slender needles, and melts at 207°, whilst the *dibromide* forms needles melt-ing at 192°. A. H.

Compound of Picric acid with Anethoïl. By G. AMPOLA (*Gazzetta*, **24**, i, 432—433).—Picric acid and anethoïl combine in alcoholic solution to form an *additive compound*,

$$C_6H_4Et·OMe,C_6H_2(NO_2)_3·OH ;$$

it crystallises in magnificent red needles, melts at 60°, and re-sembles the picrates of the naphthalene hydrocarbons in properties.
W. J. P.

Officinal Creosote from Beech and Oak. By A. BÉHAL and E. CHOAY (*Compt. rend.*, **118**, 1339—1342).—The authors apply the term "officinal creosote" to the constituents of creosote which boil between 200—220°. The creosote from beech has the same qualita-tive composition as that from oak. The monophenols are separated from the dimethyl derivatives of the diphenols after demethylating the latter by heating them with concentrated hydrochloric acid at 180°, or by passing a current of hydrogen bromide into the creosote heated at 100° in presence of a small quantity of water. The monophenols are then removed by distilling in a current of steam, and are sepa-rated by fractionation, and subsequent conversion into benzoates.

The methyl derivatives of the diphenols are separated by precipi-tation with strontium hydroxide, the precipitate being decomposed by hydrochloric acid. They are then fractionated, and, if necessary,

converted into carbonates by means of carbon oxychloride, and further separated by fractional crystallisation.

The officinal creosotes of beech and oak were thus found to contain phenol, orthocresol, metacresol, paracresol, orthoethylphenol, meta-xylenol [1 : 3 : 4], and metaxylenol [1 : 3 : 5], guaiacol, creosol, and ethylguaiacol. They also contain small quantities of sulphur deriva-tives, probably thiophenol, and a compound differing from pittacal; the latter, under the influence of ammonia and air, yields a substance which dissolves in alkalis with production of a very intense blue coloration, which is turned red by acids.   C. H. B.

Aniline and Toluidine Hydrogen Sulphates. By E. HITZLL

(*Compt. rend.*, **118**, 1335—1336).—Aniline and toluidine hydrogen sulphates are easily obtained by floating a warm saturated solution of the normal sulphate on a layer of concentrated sulphuric acid con-tained in a broad vessel. The liquid should then be cooled at 0°, or below, and after from 12 to 24 hours the upper layer of liquid becomes filled with crystals of the hydrogen sulphate. These should be at once removed, or they will gradually redissolve.

Aniline hydrogen sulphate, $NH_2Ph,H_2SO_4 + H_2O$, forms white lamellæ, which become slightly rose-coloured when exposed to air. *Orthotoluidine hydrogen sulphate* crystallises with $1H_2O$ in large, rhomboidal lamellæ. *Paratoluidine hydrogen sulphate* crystallises with $1H_2O$ in large needles, which become slightly rose-coloured when exposed to air.   C. H. B.

Action of Primary Amines of the Benzene Series on Un-symmetrical Ketonic Compounds. By L. SIMON (*Compt. rend.*, **118**, 1342—1345).—When aniline acts on pyruvic acid in presence of ether, three compounds are obtained in very unequal proportions: (1) *anilpyruvic acid*, $NPh:CMe\cdot COOH$, which melts and decomposes at 126°, is profoundly altered by cold water or alcohol, is insoluble in chloroform or ether, and only slightly soluble in warm ethylic acetate or benzene. It dissolves in concentrated sulphuric acid, the solution having a beautiful, wine-red colour, which disappears on the addi-tion of water, and changes to yellow on heating, or after standing for some time. (2) *Methylquinolinecarboxylic acid* (aniluvitonic acid), $C_9NH_5Me\cdot COOH$, a compound more stable than the preceding, from which it can be obtained by the action of water, alcohol, or heat alone; it forms beautiful, yellow crystals, soluble in warm water or alcohol, but insoluble in boiling chloroform. It melts at 246°, under-going decomposition into carbonic anhydride and methylquinoline. Concentrated sulphuric acid dissolves it, forming a yellow solution, which retains its colour even on dilution. (3) A compound which seems to have the composition $C_{12}H_{13}NO_2$. It is very stable, melts at about 188° without decomposition, and solidifies in acicular crystals, which act on polarised light; it is insoluble in cold water or benzene, slightly soluble in ether or acetic acid, very soluble in hot chloroform, from which it separates almost completely on cooling; it also dis-solves in sulphuric acid, but separates again unchanged on dilution It is not affected by boiling aqueous solutions of potassium hydroxide.

When an alkylic salt of pyruvic acid is acted on by an amine, compounds are formed of the general composition $C_5H_5O(NPh)_2 \cdot COOR$. They crystallise well, melt without undergoing decomposition, dissolve in ether, chloroform, and benzene, and also in concentrated sulphuric acid, from which they are separated unchanged on adding water.

The action of aniline on phenylglyoxylic acid in presence of ether yields white crystals of aniline phenylglyoxylate. No formation of an anilic acid takes place at the ordinary temperature, but there is some evidence that this change occurs at about 90°. If the aniline phenylglyoxylate is heated at 300°, it yields a compound which melts at 52°, dissolves in ether and alcohol, and seems to be a phenanthridine.

These experiments show that in the formation, at ordinary temperatures, of anilic derivatives of the form NPh·CRR', there are no indications of isomeric modifications similar to those observed in the oximes and some of the hydrazones. C. H. B.

Interaction of Quinones with Metanitraniline and Nitroparatoluidine. By J. LEICESTER (*Chem. News*, **69**, 291; compare Abstr., 1890, 1445).—*Quinonedimetanitranilide*, prepared by heating quinone and metanitraniline dissolved in glacial acetic acid, crystallises from a mixture of methylic alcohol and benzene, and melts at 295°. *Quinonemetanitanilide* is obtained along with the above as a bronze-coloured powder, melting at 135°.

Quinonemetahomofluorindine, $C_6H_4 < \!\!\! \frac{NH}{N} \!\!\! > \!\! C_6O_2 < \!\!\! \frac{N}{NH} \!\!\! > \!\! C_6H_4$, formed by the reduction of the dianilide with ammonium sulphide, is a brownish-black powder, melting above 360°; it gives a brown coloration with acetic acid, which changes to slaty green, and finally to mauve, on adding sulphuric acid gradually.

Quinoneparanitrotoluidide, obtained in a similar manner, is a bluish-black, crystalline powder; on reduction with ammonium sulphide, it yields a slate-coloured compound, which decomposes at 300°.

Quinonediparatoluidide is bronze-coloured, and yields, on reduction, a substance melting at 320°, and dissolving in alcohol, benzene, and acetic acid, with a dark greenish-yellow colour and green fluorescence.

Thymoquinonediorthonitranilide, from thymoquinone and orthonitraniline, crystallises from alcohol and ether in straw-coloured needles, and melts at 125°. The *phenazine*, $C_6O_2MePr < \!\!\! \frac{N}{N} \!\!\! > \!\! C_6H_4$, [O : N : Me : O : N : C_3H_7 = 1 : 2 : 3 : 4 : 5 : 6], from it forms grey needles, melting at about 320°.

Thymoquinonediparanitrotoluidide crystallises from absolute alcohol in yellowish-red plates, melting at 112°; it also forms needles.

Thymoquinoneorthomethylphenazine, $C_6O_2MePr < \!\!\! \frac{N}{N} \!\!\! > \!\! C_6H_3Me$, is a greyish-white, crystalline powder, subliming at 325°, and dissolving in acetic acid and ether with a yellow colour.

A number of crystalline compounds have also been obtained by the

reduction of anilides and toluidides with magnesium; the products are of a complex nature, and are being investigated. D. A. L.

Constitution of the Aniline Derivative of Glucose. By L. MARCHLEWSKI (*J. pr. Chem.* [2], **50**, 95—96).—A criticism of the formula assigned to this compound by v. Miller and Plöchl (Abstr., this vol., i, 413); it is claimed that Sorokin's formula (Abstr., *J. pr. Chem.* [2], **37**, 304) will equally well serve to explain the behaviour of the compound with hydrogen cyanide (compare Trans., 1893, 1137).
A. G. B.

Orthohydroxydiphenylamine. By A. DENINGER (*J. pr. Chem.*, [2], **50**, 89—90).—*Orthohydroxydiphenylamine*, $HO \cdot C_6H_4 \cdot NHPh$, is prepared by heating aniline (50 grams) with catechol (59 grams), calcium chloride (25 grams), and a little carbonic acid in an autoclave at 180° for 24 hours. The product is extracted with hydrochloric acid, and the *hydrochloride* recrystallised. The base crystallises in colourless prisms, melts at 68°, and dissolves freely in ether, glacial acetic acid, and alcohol, but only sparingly in benzene or boiling water. It reduces hot Fehling's solution, and its salts give a deep blue-black coloration with ferric chloride. A *dibenzoyl*-derivative was prepared. A. G. B.

Reaction between n-Aldoxime Ether and Phenylic Thiocarbimide. By E. BECKMANN (*Ber.*, **27**, 1957—1959).—The author has stated that the reaction between n-benzylbenzaldoxime and phenylthiocarbimide takes place according to the equation

$$\underset{\diagdown O \diagup}{CHPh \cdot N \cdot CH_2Ph} + CO\text{:}NPh = \underset{O-CO-NPh}{\overset{CHPh \cdot NH \cdot CHPh}{|}},$$
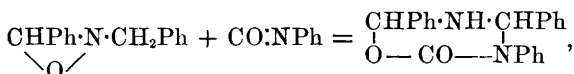
since, by the action of sodium ethoxide, the preceding additive compound is converted into the amidine, $CH_2Ph \cdot NH \cdot CPh\text{:}NPh$. A further examination of the reaction with n-aldoxime ethers containing substituents in the aldehyde- or benzyl-groups shows that the nitrogen of the phenylic isocyanate combines with the carbon atom of the aldehyde group to form compounds of the type $\underset{NPh \cdot CO}{\overset{CHPh \cdot N \cdot CH_2Ph}{|}} \diagdown O$, which, when treated with sodium ethoxide, yield amidines of the type $X \cdot \underset{\overset{||}{NPh}}{C} \cdot NH \cdot CH_2 \cdot Y$.

The following compounds have been examined: n-*benzylanisaldoxime*, $\underset{\diagdown O \diagup}{MeO \cdot C_6H_4 \cdot CH \cdot N \cdot CH_2Ph}$, m. p. 128°; n-*anisylbenzaldoxime*, $\underset{\diagdown O \diagup}{CHPh \cdot N \cdot CH_2 \cdot C_6H_4 \cdot OMe}$, m. p. 125°; n-*benzylcuminaldoxime*, m. p. 156°; and n-*cumylbenzaldoxime*, m. p. 139°. E. C. R.

The Diazotising Process. By E. BAMBERGER (*Ber.*, **27**, 1948—1953).—The author has already shown that benzenediazoic acid is

easily obtained by the action of nitric anhydride on aniline (this vol., i, 239), and the nitro-group in the side chain readily "wanders" to the nucleus. The author now shows that nitrous acid acts in the same way on primary aromatic bases, whereby nitrosamines are first formed which easily undergo isomeric change and are converted into diazo-compounds. The following aromatic bases have been examined: aniline, paratoluidine, α-naphthylamine, β-naphthylamine, ortho-, meta-, and para-nitraniline, parabromaniline, metanitroparatoluidine, paranitroorthotoluidine, orthonitroparatoluidine, metanitroorthotoluidine, and 1 : 4-nitronaphthylamine. In all cases, diazo-compounds are obtained, together with the isodiazo-compounds, as the former so readily undergo molecular change. The isodiazo-compounds are more stable according as the nature of the base is more negative. Metanitraniline and α-naphthylamine are, however, exceptions to this rule. It is important that only small quantities of the base should be employed for each experiment, as, otherwise, the prolonged duration of the action is sufficient to convert the iso-compound into the diazocompound. Thus, with 15 grams of paranitraniline, no nitroisodiazobenzene was obtained, whereas with 5 grams it was easily obtained.

From these results, the author concludes that nitrous acid acts in the same way both on primary and secondary bases, namely, to form nitrosamines, and that the difference between the two classes of aromatic bases is the result of a secondary action.

The experiments are carried out as given below for paranitraniline. A dry solution of nitrous anhydride is gradually added to paranitraniline dissolved in a mixture of equal volumes of ethylic acetate and ether at a temperature of −5°. The crystalline precipitate obtained contains diazoparanitraniline, paranitraniline, and diparadinitrodiazoamidobenzene (m. p. 233°). The ethereal filtrate is shaken with icecold water, to extract the remaining diazoparanitraniline, and then the isoparanitrodiazobenzene is extracted with very dilute ammonia.

<div align="right">E. C. R.</div>

Action of Cyanogen on α-Acidylphenylhydrazides. By O. WIDMAN (*Ber.*, **27**, 1962—1968).—α-Isobutyrylphenylhydrazide, which previously has been described as an oil, can be obtained crystalline if α-isobutyryl-β-acetylphenylhydrazide, prepared by the action of isobutyric chloride on acetylphenylhydrazide, is boiled with dilute sulphuric acid and alcohol, and the product extracted with ether. It crystallises in colourless tablets or broad needles, and melts at 46—48°.

β-Dicyan-α-isobutyrylphenylhydrazine,

<div align="center">CHMe₂·CO·NPh·N:C(CN)·NH₂.</div>

is obtained by saturating an aqueous solution of the preceding compound with cyanogen and allowing it to remain in a closed flask for two days. It melts at 150°, crystallises in beautiful, colourless leaflets or tablets, and is very easily decomposed with the formation of a triazole-compound.

β-Cyanodi-α-isobutyrylphenylhydrazine,

<div align="center">CHMe₂·CO·NPh·N:C(NH₂)·C(NH₂):N·NPh·CO·CHMe₂,</div>
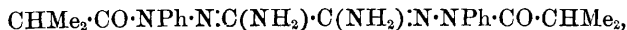
is obtained together with the preceding compound, and may be isolated by taking advantage of its being less soluble. It crystallises in small, short needles or prisms, and melts at 217°.

Cyanisopropylphenyltriazole, $NPh{<}{\substack{C(CHMe_2){:}N \\ N{=\!=\!=\!=}C{\cdot}CN}}$, is obtained

from the above dicyanisobutyrylphenylhydrazine by evaporating its alcoholic solution with a few drops of hydrochloric acid or by allowing the aqueous solution to remain exposed to the air for some time. It crystallises in colourless, six-sided tablets, or large, thin plates, and melts at 76—77°. When warmed with dilute potassium hydroxide, it yields *isopropylphenyltriazolecarboxylic acid*; this crystallises in plates containing benzene, which melt at 112°, whilst the dry substance melts at 153° with evolution of gas. The *amide* crystallises in small, colourless pyramids, and melts at 144—146°.

Bladin (Abstr., 1892, 637) has prepared a cyanisopropylphenyltriazole by heating dicyanphenylhydrazine with isobutyric anhydride; it yields a carboxylic acid, melting at 135°, and an amide, melting at 127·5°—128°. The author has repeated Bladin's experiments and finds that he was working with impure materials. The author obtained the above triazole by the action of isobutyric anhydride on dicyanphenylhydrazine.

β-Isobutyrylphenylhydrazide is obtained by the action of isobutyric chloride on phenylhydrazine. It crystallises in rhombic tablets and melts at 140°.　　　　　　　　　　　　　　　　　　　E. C. R.

Diacid Anilides. By G. TASSINARI (*Gazzetta*, **24**, i, 444—449; compare this vol., i, 285).—On heating diacetanilide with acetic acid, it is partially converted into acetanilide, acetic anhydride being formed.

Parachlorodiacetanilide, $C_6H_4Cl{\cdot}NAc_2$, is prepared by heating parachloracetanilide with acetic anhydride and anhydrous sodium acetate; it is soluble in benzene, alcohol, or ether, and separates in large crystals melting at 66—67°. One acetyl-group is eliminated on treating it with N/10 soda at 70°.

Metanitrodiacetanilide, $NO_2{\cdot}C_6H_4{\cdot}NAc_2$, is formed on heating metanitroacetanilide with acetic anhydride and sodium acetate; it is very soluble in benzene or ether, and is obtained in large, colourless crystals melting at 76—77°. On heating with N/10 soda, it is converted into metanitroacetanilide; this forms small, colourless crystals melting at 152—153°, not yellow crystals melting at 140—141°, as stated by Meyer and Stüber (*Annalen*, **165**, 173).

Monacetyloxanilide, $C_{16}H_{14}O_3N_2$, is prepared by heating oxanilide with acetic anhydride and sodium acetate in a reflux apparatus; it is a crystalline powder melting at about 197—198°. When heated with N/10 soda, it is converted into diphenylethenylamidine.

Ethenylparaditolylamidine, $C_{16}H_{16}N_2$, is obtained by heating acetylparaoxatoluidide with N/10 soda; it crystallises in colourless needles and melts at 120—121°.　　　　　　　　　　　　　　　　W. J. P.

Study of the Mono- and Bi-basic Hydroxy-acids. By C. A. BISCHOFF (*Annalen*, **279**, 153—188).—In this paper, the author sum-

marises and discusses the results described in papers by Walden and himself (the two following abstracts, and this vol., i, 493, 495, 496, 525) in accordance with his "dynamical hypothesis" (Abstr., 1891, 892).

On heating potassium chloromalonate, potassium chloride is formed and carbonic anhydride evolved; no other product could be isolated. *Potassium chloromethylmalonate* is a colourless, crystalline salt which behaves similarly to the preceding when heated; if it is heated in heavy petroleum, small quantities of acrylic acid (?) are formed.

Propionylparatoluidide, $C_6H_4Me\cdot NH\cdot CO\cdot CH_2Me$, crystallises in colourless tablets melting at 126°. *Isobutyrylorthotoluidide* is obtained in colourless needles melting at 115—116° and is identical with a substance prepared by Tigerstedt (Abstr., 1893, i, 51). *Isobutyrylparatoluidide* crystallises in colourless leaflets melting at 109°. *Phenylacetylorthotoluidide*, $C_6H_4Me\cdot NH\cdot CO\cdot CH_2Ph$, is obtained in colourless needles melting at 159°.

Ladenburg's formylorthotoluidide (*Ber.*, **10**, 1128) is really oxalorthotoluidide: when heated with phosphorus pentachloride, it yields *oxalotoluidimidochloride*, $C_6H_4Me\cdot N:CCl\cdot CCl:N\cdot C_6H_4Me$, in long, yellow needles melting at 130—131°. W. J. P.

Derivatives of Malic Acid. By C. A. Bischoff and P. Walden (*Annalen*, **279**, 130—137; compare Bischoff, Abstr., 1891, 1220).— Anilidosuccinanil and dichlormaleïndianil (compare Bearis, *Inaug. Diss.*, Bonn, 1892) are formed on treating malic dianilide with phosphorus pentachloride. The succinanil is also obtained by heating maleïc acid with aniline and water; it is then accompanied by *aniline maleate*, $C_2H_2(COOH)_2(NH_2Ph)_2$, a crystalline substance melting at 143—144° (compare Osipoff, Abstr., 1889, 124).

The fumaric diparatoluidide already described by Bischoff (Abstr., 1891, 1220) and Giustiniani's paratolylfumaramide (Abstr., 1893, i, 264), are, in all probability, maleïc diparatoluidide. Phosphorus pentachloride, in absence of a diluent, acts on malic diparatoluidide with formation of paratoluidine hydrochloride and *chlorosuccinyltolyl*, $\begin{matrix} CHCl\cdot CO \\ CH_2—CO \end{matrix}>N\cdot C_6H_4Me$, which crystallises in slender needles melting at 156—158°. On treating malic diparatoluidide, suspended in benzene, with phosphorus pentachloride, *chlorosuccinic diparatoluidide*, $C_6H_4Me\cdot NH\cdot CO\cdot CH_2\cdot CHCl\cdot CO\cdot NH\cdot C_6H_4Me$, is obtained. It decomposes without melting at above 250°, and is accompanied by other substances which could not be purified. W. J. P.

Derivatives of Tartaric Acid. By C. A. Bischoff and P. Walden (*Annalen*, **279**, 138—152).—Tartranilide melts at 263—264°, whilst diacetyltartranilide melts at 214—215°; the melting points given by Polikin (Abstr., 1892, 54) are erroneous. On treating tartranilide, suspended in benzene, with phosphorus pentachloride, dichlormaleïndianil and *anilanilidochlorosuccinic monanilide*, (?)

$$NPh:C(COOH)\cdot CCl(NHPh)\cdot CO\cdot NHPh,$$
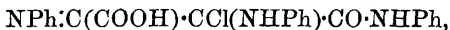
are formed; the latter melts at 170—178°, and was not obtained pure. The supposed piperazine derivative, described by Bischoff and others

(Abstr., 1893, i, 54, 564), is also formed in this reaction; numerous unsuccessful attempts were made to prepare this compound from dianilidosuccinic acid, and so throw light on its constitution, which is still problematic. *Chlorofumaric dianilide,*

$$NHPh \cdot CO \cdot CH \cdot CCl \cdot CO \cdot NHPh,$$
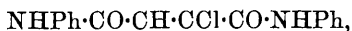
is not formed when phosphorus pentachloride acts on tartranilide, but it is readily produced by the interaction of chlorofumaric chloride and aniline; it crystallises in colourless needles melting at 186°.

The four substances next described are formed on treating tartaric paratoluidide with phosphorus pentachloride.

1. *Toluidochloromaleintolyl,* $C_6H_4Me \cdot NH \cdot C \overset{\overset{\text{CCl} \cdot \text{CO}}{|}}{\underset{}{}} {-}CO \hspace{-0.3em}>\hspace{-0.3em} N \cdot C_6H_4Me$, crystallises in yellow prisms melting at 198—199°; this substance may equally well be the tautomeric tolylchlorosuccintolyl.

2. A *trichloro*-derivative,

$$C_6H_4Me \cdot N \vdots CCl \cdot CCl \vdots CCl \cdot CO \cdot NH \cdot C_6H_4Me \ (?),$$

is obtained in white needles melting at 192—192·5°.

3. *Tolyltoluidochlorosuccinic monotoluidide,*

$$C_6H_4Me \cdot N \vdots C(COOH) \cdot CCl(NH \cdot C_6H_4Me) \cdot CO \cdot NH \cdot C_6H_4Me,$$

crystallises in yellow needles melting at 186°.

4. A *substance* of the composition $C_{25}H_{31}N_3ClPO_7$, which forms an amorphous, colourless powder melting at 220—221°; it is readily decomposed by dilute soda.

Tartaric di-α-naphthalide,

$$C_{10}H_7 \cdot NH \cdot CO \cdot CH(OH) \cdot CH(OH) \cdot CO \cdot NH \cdot C_{10}H_7,$$
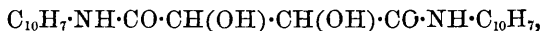
prepared by heating tartaric acid with α-naphthylamine at 180°, crystallises in colourless needles melting at 214°. It readily yields a *diacetyl*-derivative which forms colourless needles melting at 260°. On heating the naphthalide with benzoic chloride, the *dibenzoyl*-derivative is obtained; it melts at 215—217° with decomposition, and is accompanied by benzoyl-α-naphthalide.

Tartaric di-β-naphthalide crystallises in silvery leaflets melting at 280°. Its *diacetyl*-derivative is obtained in colourless needles melting at 240°, whilst the *dibenzoyl*-derivative forms white, nodular crystals melting at 179—180°; the latter substance is accompanied by benzoyl-β-naphthalide. W. J. P.

Derivatives of "Phenocoll," of Paramidophenetoïl, and of Anisidine. By F. NICOLA (*Chem. Centr.*, 1894, i, 418—419; from *Ann. Chim. Farm.*, **18**, 353—365).—The knowledge of "phenocoll," $OEt \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_2 \cdot NH_2$, and its derivatives being somewhat uncertain, the author has restudied the subject. The free base was prepared from the commercial chloride. It forms white needles soluble in alcohol and in boiling water; the crystals contain $1H_2O$, which they lose at 80—90°, and the anhydrous base then melts at 99·5°; at a slightly higher temperature ammonia is evolved,

leaving a residue which gives a fine, reddish-violet coloration with ferric chloride The platinochloride forms anhydrous, yellow prisms, whilst the chloride crystallises with 1 mol. aq. "*Cyanacetophenocoll*," $OEt \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_2 \cdot NH \cdot CO \cdot CH_2 \cdot CN$, obtained by the action of cyanacetic acid on phenocoll, yields white crystals melting at 28°. When oxidised with potassium permanganate, it yields "*phenocolloxamic acid*," $OEt \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_2 \cdot NH \cdot CO \cdot COOH$, forming small, white crystals soluble in alcohol or water; it melts and decomposes at 202°.

Cyanacetoparamidophenetoil, $OEt \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_2 \cdot CN$, is obtained by the action of ethylic cyanacetate on paramidophenetoïl. It crystallises in white needles melting at 180—181°. When oxidised with potassium permanganate, it yields *ethoxyphenyloxamic acid*,

$$OEt \cdot C_6H_4 \cdot NH \cdot CO \cdot COOH,$$

in small, white crystals melting and decomposing at 180°.

Cyanacetoanisidine, $OMe \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_2 \cdot CN$, forms glistening, white needles melting at 136°; it yields *methoxyphenyloxamic acid* on oxidation.

Diethoxyphenylmalonamide, $CH_2(CO \cdot NH \cdot C_6H_4 \cdot OEt)_2$, and *dimethoxyphenylmalonamide* are formed as bye-products during the preparation of the two last-named cyano-derivatives.   L. T. T.

Amidoguanidine. By G. PELLIZZARI and G. CUNEO (*Gazzetta*, **24**, i, 450—467; compare Pellizzari, Abstr., 1892, 579).—Amidoguanidine is readily prepared by heating an alcoholic solution of hydrazine hydrochloride with cyanamide in a reflux apparatus (compare Thiele, Abstr., 1892, 1295).

Orthotolylamidoguanidine, $NH_2 \cdot C(NH) \cdot NH \cdot NH \cdot C_7H_7$, is prepared by boiling an alcoholic solution of orthotolylhydrazine hydrochloride and cyanamide. A poor yield of the base is obtained on heating orthotolylhydrazine hydrochloride and guanidine carbonate at 150—160°. The *hydrochloride* crystallises in large, red prisms melting at 212°; it is soluble in alcohol or water. The *nitrate* crystallises in colourless needles and melts at 206·5°. The *platinochloride* is obtained in beautiful, yellow needles, whilst the *picrate* crystallises in massive, yellow needles melting at 206°.

Paratolylamidoguanidine is prepared in a similar way to its ortho-isomeride. Its *hydrochloride* crystallises in transparent scales melting at 196·5°, and is very soluble in water or alcohol. The *nitrate* is obtained in colourless laminæ melting at 181°, and is sparingly soluble in water. The *platinochloride* separates from its aqueous solution in red crystals, whilst the *picrate* crystallises in yellow needles melting at 212°.

α-Naphthylamidoguanidine, $NH_2 \cdot C(NH) \cdot NH \cdot NH \cdot C_{10}H_7$, prepared from cyanamide and *α*-naphthylhydrazine hydrochloride, yields a *hydrochloride* which crystallises in small, colourless needles melting at 166°. The *platinochloride* is obtained as a yellow, crystalline powder.

β-Naphthylamidoguanidine hydrochloride separates from aqueous solution in minute crystals which decompose at 250—260°; it is very

soluble in alcohol, sparingly so in cold water. The *nitrate* forms small crystals melting at 230°, and is sparingly soluble in water. The *platinochloride* is a red, crystalline powder, whilst the *picrate* is a yellow, crystalline powder sparingly soluble in water.

The salts of the tolyl- and naphthyl-amidoguanidines reduce ammoniacal silver nitrate, and do not react with benzaldehyde. The free bases could not be isolated, as they decompose as soon as formed.

Ethylphenylamidoguanidine, $NH_2 \cdot C(NH) \cdot NH \cdot NEtPh$, is prepared by heating α-ethylphenylhydrazine hydrochloride with cyanamide; the *platinochloride* is obtained as a yellow, flocculent precipitate melting and decomposing at 150°. The *picrate* crystallises in red prisms melting at 224°; it is accompanied by another *picrate* which crystallises in transparent scales melting at 269°.

Phenylamidomethylguanidine, $NH_2 \cdot C(NH) \cdot NMe \cdot NHPh$, is obtained by heating hydrazomethylphenyl hydrochloride with cyanamide in alcoholic solution. The *hydrochloride* crystallises in white, transparent prisms, melts at 227°, and is very soluble in water or alcohol; the *platinochloride* is obtained in thin, red needles. The *nitrate*, which forms white crystals melting and decomposing at 105—106°, is very soluble in water or alcohol. The *picrate* crystallises in yellow needles melting and decomposing at 215°. W. J. P.

Guanazole and its Derivatives. By G. PELLIZZARI (*L'Orosi*, **17**, 143—155, 185—192; compare Abstr., 1892, 356).—*Paratolylguanazole*,

$$\begin{matrix} C(NH) \cdot NH \\ | \\ NH \cdot C(NH) \end{matrix} \Big> N \cdot C_7H_7,$$ is obtained, with evolution of ammonia, on

heating paratolylhydrazine hydrochloride with dicyanodiamide in molecular proportion, at 140—200°; it crystallises in yellowish prisms, melts at 172°, and is soluble in water or alcohol. It dissolves in acids, and is reprecipitated on adding potash; this fact is taken advantage of in its purification. The *hydrochloride*, $C_2N_5H_4 \cdot C_7H_7,HCl$, crystallises in white needles melting at 256°, and is readily soluble in water or alcohol. The *platinochloride*, $(C_9N_5H_{11})_2,H_2PtCl_6$, crystallises in lustrous, yellow needles melting at 93°. The *nitrate*, $C_9N_5H_{11},HNO_3$, separates from water in aggregates of small needles melting at 155°. The *picrate* crystallises in transparent, yellow needles melting at 218°.

Orthotolylguanazole, $C_2N_5H_4 \cdot C_7H_7$, is prepared by a process similar to that which yields its para-isomeride; it forms large, reddish crystals melting at 159°, and is soluble in water or alcohol. The *hydrochloride* separates in large, hard crystals melting at 202°. The *nitrate* crystallises in prisms melting at 226°, and is sparingly soluble in water. The *picrate* separates from its aqueous solution in small crystals melting at 212°.

β-*Naphthylguanazole*, $C_2N_5H_4 \cdot C_{10}H_7$, crystallises in transparent laminæ melting at 199°; it is soluble in alcohol, but only sparingly so in water. The *hydrochloride* crystallises in thin, white needles melting at 255°. The platinochloride is obtained in very minute, yellow crystals, and is sparingly soluble in water.

Phenylmethylguanazole, $\begin{matrix} C(NH) \cdot NMe \\ | \\ NH \cdot C(NH) \end{matrix} \Big> NPh$, is prepared by heating

methylphenylhydrazine hydrochloride with dicyanodiamide at 130°; it forms small, white crystals melting and decomposing at 208°, and is soluble in water or alcohol. The *hydrochloride* is very soluble in water, and crystallises in transparent prisms which do not melt at 275°; the *platinochloride* crystallises in small, yellow needles, whilst the *nitrate* forms large, yellowish crystals which, at 245°, melt and decompose.

Guanazole, $\dfrac{\mathrm{C(NH)\cdot NH}}{\mathrm{NH\cdot C(NH)}}{>}\mathrm{NH}$, is most readily prepared by heating hydrazine monohydrochloride and dicyanodiamide with alcohol at 100°; only a small yield of guanazole is obtained on heating without alcohol. It crystallises from water in beautiful, transparent, monosymmetric crystals melting at 206°; $a : b : c = 4\cdot2743 : 1 : 2\cdot4967$. $\beta = 88°\ 14'$. It is soluble in water or alcohol, but insoluble in ether, chloroform, or benzene; its aqueous solution has a feebly alkaline reaction, and, on the addition of potassium nitrite and acid, deposits a yellow *nitroso*-derivative. On crystallising a solution of guanazole in hydrochloric acid, the dihydrochloride is obtained in long needles melting at 145°; it has a strongly acid reaction, and dissociates in aqueous solution. The *monohydrochloride* is obtained by repeatedly evaporating the aqueous solution of the acid salt with water or alcohol; it crystallises in white prisms melting at 100°, and is very soluble in water or alcohol; no platinochloride could be prepared. The *sulphate*, $C_2N_5H_5,H_2SO_4,2H_2O$, separates from its solution in small, white prisms which lose their water at 100°; the *nitrate*, $C_2N_5H_5,HNO_3$, is obtained in very small crystals melting at 165°, and is very soluble in water; the *picrate*, $C_2N_5H_5,C_6H_3N_3O_7$, crystallises in flat needles melting at 245°. *Guanazole silver nitrate*, $C_2N_5H_5,AgNO_3$, is obtained by adding silver nitrate to an aqueous solution of guanazole; it forms white flocks soluble in nitric acid or ammonia, and slowly blackens on exposure to light; *guanazole copper sulphate*, $C_2N_5H_5,CuSO_4,5H_2O$, is a green, crystalline precipitate, obtained on adding copper sulphate to a solution of guanazole; it loses its water at 200°. A *substance* of the composition $2C_2N_5H_4HgCl,HgCl_2$, is precipitated as a white powder on adding mercuric chloride to an aqueous solution of guanazole; it is insoluble in water, but dissolves in acids. On dissolving it in warm hydrochloric acid, and cooling, a *substance* of the composition $2(C_2N_5H_5,HCl),HgCl_2$ separates in long, white needles; whilst if crystallised from water, nodular masses of white needles of a *substance* of the composition $C_2N_5H_5,HCl,HgCl_2$ separate.

<div align="right">W. J. P.</div>

Synthesis of Hydroxy-aromatic Bases. By M. NENCKI (*Ber.*, **27**, 1969—1979).—The condensation products of chloracetopyrogallol or chloracetocatechol and quinoline are readily decomposed by alkalis; the corresponding derivatives of isoquinoline, however, are more stable. *Catecholglycoisoquinoline*, $\mathrm{OH\cdot C_6H_3}{<}\dfrac{\mathrm{CO\cdot CH_2}}{\mathrm{O-NC_9H_7}} + 2H_2O$, is prepared from the chloride (see below) by the action of alkalis or ammonia, and forms glittering, orange-coloured crystals which darken on drying; the base gives a red coloration with highly dilute ferric

chloride, whilst with excess of the latter the colour is green; both the chloride and the base dye cotton mordanted with iron, aluminium, or chromium salts, black, yellow, or reddish-brown respectively. The *chloride*, $C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot C_9NH_7Cl + \frac{1}{2}H_2O$, is prepared from chloracetocatechol and isoquinoline, and forms colourless crystals. The *sulphate, tartarate*, and *oxalate* are crystalline, and are decomposed completely by the action of alkalis in excess, indicating that the base is actually an anhydride, as represented above. *Pyrogallolglycoisoquinoline* crystallises in small, rose-coloured hexagonal plates, and is decomposed by boiling with water or exposure to air. The *hydrochloride*, $C_6H_2(OH)_3 \cdot CO \cdot CH_2 \cdot C_9NH_7$, HCl, crystallises in slender, colourless needles. The *platinochloride* crystallises with 3 or 4 H_2O, according to circumstances, in small, yellow needles. *Pyrogallolglycotetrahydroquinoline*, $C_6H_2(OH)_3 \cdot CO \cdot CH_2 \cdot C_9NH_{10}$, is prepared in a similar manner to the preceding compounds, and is deposited from alcohol in yellow crystals melting at 177—178°. It forms amorphous, yellow, metallic salts, and does not combine with acids. The *sulphonic acid*, $C_{17}H_{16}NO_4 \cdot SO_3H$, crystallises in colourless plates melting at 188°. By the action of phenylhydrazine on the tetrahydroquinoline derivative, under the most varied conditions, the compound,

$$C_6H_2(OH)_3 \cdot C(N \cdot NHPh) \cdot CH_2 \cdot NH \cdot NHPh,$$

is formed; it crystallises in slender, yellow, silky, lustrous needles melting at 214—215°. *Catecholglycotetrahydroquinoline*, $C_{17}H_{17}NO_3$, is prepared in a similar manner to the pyrogallol derivative, and crystallises in yellow, lustrous plates melting at 170°. The *sulphonic acid*, $C_{17}H_{16}NO_3 \cdot SO_3H$, is crystalline, and gives a deep-red coloration with ferric chloride or nitric acid. Tetrahydroisoquinoline is oxidised by the action of the chloroketones which then combine with the resulting isoquinoline in the manner described above.

Vanillethylenequinoline, $OH \cdot \overset{4}{C}_6H_3(\overset{3}{OMe}) \cdot CH{:}CH \cdot \overset{1}{C_9NH_6}$, is prepared by the action of hydroxymethoxybenzaldehyde [CH : OMe : OH = 1 : 3 : 4] on quinaldine, and crystallises in glittering, yellow plates melting at 182°. It dissolves sparingly in acids, forming crystalline salts, is insoluble in alkali carbonates, and gives a yellowish-red coloration with ferric chloride. The *sodium salt* is yellow and crystalline. The *hydrochloride* crystallises in red needles with $2\frac{1}{2}H_2O$; the *platinochloride* is red and amorphous. The *dibromide*, $C_{18}H_{15}Br_2O_2N$, forms yellow crystals, it darkens at 220°, but does not melt, and dissolves in concentrated sulphuric acid without evolution of hydrogen bromide. On reduction, by means of sodium in alcoholic solution, the base is converted into *vanillethyltetrahydroquinoline*, $OH \cdot C_6H_3(OMe) \cdot CH_2 \cdot CH_2 \cdot C_9NH_{10}$, which forms colourless crystals melting at 88°, and is not poisonous. The yield is good. The *hydrochloride* crystallises in pale yellow needles, and gives a characteristic red coloration with ferric chloride or dilute nitric acid. *Piperonethylenequinoline* is prepared in a similar manner from quinaldine and piperonal; it crystallises in pale yellow needles, melts at 155°, and gives no coloration with ferric chloride. The *hydrochloride* crystallises in red needles. Opianic acid and quinaldine condense,

forming *opianylquinaldine*, $C_{20}H_{17}NO_4$, which crystallises with $1H_2O$ in colourless needles, melts at 103°, becomes yellow and anhydrous at 105°, and melts again at 174—175°. It is readily soluble in dilute acids, insoluble in alkalis, but is hydrolysed by the prolonged action of soda. The compound is optically inactive, its constitution and relationship to berberine, with which it is isomeric, are being investigated. The *hydrochloride* crystallises in yellow needles. Two *platinochlorides* were obtained, the one, $(C_{20}H_{17}NO_4)_2,H_2PtCl_6$, is yellow and amorphous, the other forms hydrated crystals.

Crystalline condensation products of dihydroxybenzaldehyde [$CH:OH:OH = 1:3:4$] and furfuraldehyde with quinaldine have also been prepared. In common with piperonethylenequinoline, they are reduced to colourless, crystalline bases, when treated in alcoholic solution with sodium; the yield is almost quantitative.

J. B. T.

Refraction Constants of Coumarone and of Indene. By G. GENNARI (*Gazzetta*, **24**, i, 468—474).—The author has determined the refraction constants of coumarone for the rays H_α, H_β, H_γ, and D at 16·3°. The values for the line H_α are for $P \dfrac{\mu_{H_\alpha} - 1}{d}$, 60·6 (observed) and 60·2 (calculated); for $P \dfrac{\mu^2_{H_\alpha} - 1}{(\mu_{H_\alpha} + 2)d}$, 34·89 (observed) and 34·78 (calculated).

Some measurements were also made with indene; the sample used, however, contained oxygen, and the results obtained are not so trustworthy as those given by Perkin (Trans., 1894, 228). W. J. P.

Benzoic Peroxide, an Oxidation Product of Benzaldehyde. By E. ERLENMEYER, Jun. (*Ber.*, **27**, 1959—1962).—The author has obtained benzoic peroxide from the mother liquor of the condensation products of benzaldehyde with acetic anhydride, after it had been exposed to the air for some time. Benzoic peroxide is easily obtained by allowing a mixture of benzaldehyde and acetic anhydride, mixed with sand, to remain exposed to the air for three days. The product has a strong odour of ozone, which can be easily detected by potassium iodide and starch, and yields benzoic peroxide when extracted with warm ether. Benzoic peroxide is also obtained in the same way from a mixture of benzaldehyde and benzoic anhydride.

The author was unable to obtain benzoic peroxide from benzaldehyde when acetic acid, benzene, ether, or ethylic benzoate was substituted for acetic anhydride. E. C. R.

Preparation of Diphenylacetaldehyde and Synthesis of Tolane Derivatives. By P. FRITSCH (*Annalen*, **279**, 319—323; compare this vol., i, 502, 507).—Dichloracetal condenses with hydrocarbons to form asymmetric disubstitution derivatives of dichlorethane, $CHX_2 \cdot CHCl_2$, which, on treatment with potash, pass into the corresponding derivatives of monochlorethylene, $CX_2:CHCl$. These again, when acted on with sodium ethoxide, react in two different ways.

Diphenylmonochlorethylene yields, as chief product, diphenylvinyl ethyl ether, $CPh_2:CH\cdot OEt$, accompanied by a small amount of tolane, $CPh:CPh$, whereas ditolyl-, dianisyl-, and diphenetyl-monochlorethylene do not yield substituted vinyl ethyl ethers, but are entirely converted into the corresponding para-substituted tolanes.

<div align="right">A. H.</div>

Metahydroxyacetophenone. By P. BIGINELLI (*Gazzetta*, **24**, i, 437—444).—*Metamidoacetophenone*, $C_6H_3Ac\cdot NH_2$, is prepared by reducing metanitroacetophenone with tin and hydrochloric acid; it crystallises in thin, yellow laminæ, and melts at 93—94°. The *hydrochloride* crystallises in micaceous laminæ, melting and decomposing at 167—168°; it is very soluble in water, and is partly converted into another hydrochloride on boiling with alcohol. No platinochloride could be prepared.

Metahydroxyacetophenone, $C_6H_3Ac\cdot OH$, is obtained by diazotising the hydrochloride of the preceding base with potassium nitrite; the diazo-compound gradually decomposes, yielding the hydroxy-derivative, which is ultimately obtained in small needles melting at 92—93°. It has a phenolic odour, and is soluble in dilute soda, being precipitated from the solution by carbonic anhydride. It gives no colour reaction with ferric chloride. No hydrazone could be isolated.

Metahydroxyphenylmethylcarbinol, $OH\cdot C_6H_3\cdot CHMe\cdot OH$, is formed on reducing, with sodium amalgam, the preceding compound dissolved in methylic alcohol; it crystallises in small prisms, and melts at 116—117°.

<div align="right">W. J. P.</div>

Resacetophenone. By A. WECHSLER (*Monatsh.*, **15**, 239—248).— When dihydroxyacetophenone (resacetophenone) is treated with alkaline permanganate, it is only partially converted into acetic acid and a resinous substance, which has not been further examined. The greater part of the original substance is recovered unaltered. When treated with alcoholic soda on the water-bath, only a very small quantity of acetic acid is formed, and this is probably due to the oxidising action of the alkali.

Dibromodihydroxyacetophenone is obtained by adding excess of bromine to an acetic acid solution of dihydroxyacetophenone. It separates in small, lustrous crystals, melts at 173—174°, and turns red on exposure to air.

Dihydroxyacetophenoneoxime separates in pale, yellowish-green crystals, melts and decomposes at 198—200°, and, with ferric chloride, gives a coloration similar to that of dihydroxyacetophenone.

Diethoxyacetophenone, obtained in the usual way, crystallises in triclinic needles, melts at 78°, is insoluble in water, alkali hydroxides and carbonates, and gives no coloration with aqueous ferric chloride. It yields a crystalline brominated derivative, and gives a green solution with concentrated nitric acid. When heated with concentrated hydrochloric acid at 160°, it is converted into a brownish-red dye, which is insoluble in alkali carbonates, but dissolves in alkali hydroxides, yielding a beautiful bright-red solution.

<div align="right">E. C. R.</div>

Action of Nitrosyl Chloride on Menthone. By A. BAEYER and
O. MANASSE (*Ber.*, **27**, 1912—1915).—Claisen and Manasse have
shown that, under suitable conditions, camphor is readily converted
by amylic nitrite into the isonitrosoketone, $CH{<}_{CPr^{\beta} \cdot CO}^{CH \cdot CMe}{>}C{:}N{\cdot}OH$,
from which the corresponding camphorquinone may be prepared
(Abstr., 1893, i, 479). The authors have endeavoured to convert
the analogous menthone into similar derivatives, but found that in
this case the action proceeds in a different manner, a *tertiary nitroso-
derivative*, $CH_2{<}_{CPr^{\beta}(NO) \cdot CO}^{CH_2 - CHMe}{>}CH_2$, being obtained. It is prepared
by adding amylic nitrite very slowly to a mixture of menthone and
hydrochloric acid, then shaking the product with ice, and adding
dilute soda; the residual oil contains undissolved nitrosomenthone,
which, after recrystallisation from ether, forms lustrous needles, and
melts at 112·5°, undergoing decomposition. The chief product of the
action of the amylic nitrite is, however, found in the soda solution, and
is an open chain acid, derived from nitrosomenthone by the addition
of the elements of water; it has the constitution,

$$CHMe_2 \cdot C(NOH) \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot COOH,$$
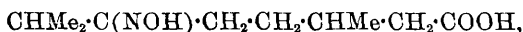
the opening of the chain taking place between the carbonyl group,
and the carbon atom combined with the isopropyl group. This acid,
dimethyl-2 : 6-oximido-3-octanic acid, forms crystals which melt at
98·5°, and, on boiling with dilute acids, yields the corresponding
ketonic acid, which is identical with the oxymenthylic acid described
by Arth (Abstr., 1886) and Mehrländer (*Inaug. Diss. Leipsig*, 1887).
                                                              H. G. C.

**Removal of Hydrogen from Hydrogenised Benzenecarb-
oxylic Acids.** By A. EINHORN and R. WILLSTÄTTER (*Annalen*, **280**,
88—95).—The method described consists in heating the acid for two
hours at 200° with the theoretical quantity of bromine, calculated on
the scale of one molecular proportion of the halogen for every two
atoms of added hydrogen. Paratoluic acid is obtained almost
quantitatively from Δ^1-tetrahydroparatoluic acid (following abstract)
and from hexahydroparatoluic acid (paraoctonaphthenic acid,
Markovnikoff, this vol., i, 245), whilst Δ^1-tetrahydroterephthalic
acid and fumaroïd hexahydroterephthalic acid yield terephthalic acid.
Less satisfactory results are obtained with ortho- and metahexa-
hydrotoluic acids, and it does not appear that carboxy-derivatives
of other polymethylene systems behave in this way.   M. O. F.

Hydrogenised Paratoluic Acids. By A. EINHORN and R.
WILLSTÄTTER (*Annalen*, **280**, 159—165 ; compare Abstr., 1893, i,
713).—Hexahydroparatoluic acid (this vol., i, 245) was brominated
by the method described by v. Baeyer (Abstr., 1888, 1075), sufficient
bromine being employed for the introduction of one atom of the halo-
gen. *α-Bromohexahydroparatoluic acid* prepared in this way melts
at 71—72°; it is scarcely soluble in water, but dissolves readily in all
other ordinary solvents. Dissolved in soda, it remains unattacked
by a cold solution of potassium permanganate.

Δ^1-*Tetrahydroparatoluic acid* is obtained from the foregoing compound on removing hydrogen bromide by means of hot quinoline, the substance being purified by distillation in a current of steam ; it forms odourless needles and plates, and melts at 132°. Potassium permanganate is immediately decolorised by its alkaline solution, although it remains unattacked when boiled with potassium ferricyanide, and has no reducing action on cupric acetate or an ammoniacal silver solution. The *amide* crystallises in flat, lustrous needles, and melts at 148°. M. O. F.

Paramethylenedihydrobenzoic acid. By A. EINHORN and R. WILLSTÄTTER (*Annalen*, **280**, 96—159; compare Abstr., 1893, i, 713, and Einhorn and Tahara, Abstr., 1893, i, 378).—The reduction of this acid has yielded results which cause the authors to so far modify the view of its constitution adopted by Einhorn and Tahara

(*loc. cit.*) as to represent it by the formula $C\diagup\begin{smallmatrix}CH \cdot CH_2\\-CH_2-\\CH:CH\end{smallmatrix}\diagdown C \cdot COOH$.

It is, therefore, $\Delta^{2,\ 4}$-paramethylenedihydrobenzoic acid, this conclusion having been arrived at on the following grounds :—The hydrogenised acid, $C_8H_{14}O_2$, obtained by reducing paramethylenedihydrobenzoic acid does not agree in properties with any of the isomeric hexahydroparatoluic acids, and the product of incomplete reduction is found to be quite unlike its isomeride, Δ^1-tetrahydroparatoluic acid (preceding abstract). On the other hand, since paratoluic acid is formed when 2HBr are eliminated from the dihydrobromide of paramethylenedihydrobenzoic acid, it is clear that the latter must belong to the series of hydrogenised paratoluic acids, especially as, on reduction, it yields Markovnikoff's liquid hexahydroparatoluic acid. Moreover, although the existence of an unsaturated dihydrobromide appears inconsistent with the presence of only two double linkings in the original substance, it is reasonable to suppose that the central methylene group is but loosely attached. Of the carbon atoms to which it is united, one occupies the para-position relatively to the carboxyl group, three alternatives offering themselves in the choice of a position for the second, as represented by the following types :
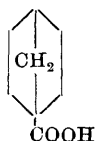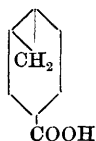
Evidence is brought forward against the first and second of these, the acceptance of the third being quite justified by its complete accordance with the results of the authors' experiments. Of the two forms,

$$CH\diagup\begin{smallmatrix}CH:CH\\-CH_2-\\CH:CH\end{smallmatrix}\diagdown C \cdot COOH \quad \text{and} \quad C\diagup\begin{smallmatrix}CH \cdot CH_2\\-CH-\\CH:CH\end{smallmatrix}\diagdown C \cdot COOH,$$
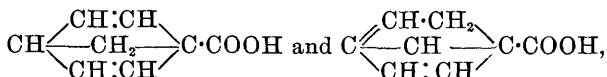
the latter best explains the formation of Δ^3-tetrahydroparatoluic acid

by the displacement of hydrogen by bromine in the intermediate Δ^3-dihydrobromide. Finally, in regard to the breaking-down of the molecule, this can obviously take place either at a linking common to both pentamethylene systems, giving rise to hydrogenised paratoluic acids, or at some point in the periphery, in which case a substituted pentamethylenecarboxylic acid is formed.

The analogy existing between anhydroecgonine and tropidine, if extended to paramethylenedihydrobenzoic acid and tropilidene, suggests the representation of the latter by the formula

$$C \left\langle \begin{array}{c} \nearrow CH \cdot CH_2 \\ -CH_2- \\ \searrow CH : CH \end{array} \right\rangle CH$$
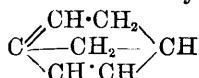
(compare Merling, Abstr., 1892, 359).

The following facts appear for the first time :—The *tetrabromide* of paramethylenedihydrobenzoic acid, $C_7H_7Br_4 \cdot COOH$, is obtained pure by repeated crystallisation from a mixture of formic and glacial acetic acids, and melts at 174—175°; its alkaline solution immediately decolorises potassium permanganate, indicating its unsaturated character.

Γ^α-Δ^2-1 : 4-*Ethylcyclopentenecarboxylic acid*, $CHEt \left\langle \begin{array}{c} CH_2 \cdot CH \cdot COOH \\ CH : CH \end{array} \right.$,

obtained by the reduction of paramethylenedihydrobenzoic acid with sodium amalgam at the ordinary temperature, has already been fully described as " tetrahydroparatoluic acid " (Abstr., 1893, i, 713).

Γ^β-Δ^2-1 : 4-*Ethylcyclopentenecarboxylic acid* was not obtained in the solid state, and could only be distinguished from the foregoing acid by means of the *amide*, which melts at 185°.

Δ^1-1 : 4-*Ethylcyclopentenecarboxylic acid*, $CHEt \left\langle \begin{array}{c} CH_2 \cdot C \cdot COOH \\ CH_2 \cdot CH \end{array} \right.$, may

be prepared in three ways : the reduction of a hot solution of paramethylenedihydrobenzoic acid, the action of warm caustic alkalis on the Γ^α-Δ^2-acid, and the removal of 1 mol. HBr from α-brom-1 : 4-ethylcyclopentanecarboxylic acid (see below). It melts at 47—50° (compare Abstr., 1893, i, 713), and distils undecomposed at 260—265°; its behaviour towards bromine and potassium permanganate is similar to that of the preceding acids, from which it may be distinguished however by its stability towards an alkaline solution of potassium ferricyanide.

1 : 4-*Ethylcyclopentanecarboxylic (ethylpentamethylenecarboxylic) acid*, $CHEt \left\langle \begin{array}{c} CH_2 \cdot CH \cdot COOH \\ CH_2 \cdot CH_2 \end{array} \right.$, is best prepared by reducing paramethylenedihydrobenzoic acid with sodium dissolved in amylic alcohol. It is a colourless, highly refractive oil, which boils unchanged at 245—248° (uncorr.), and does not solidify at $-20°$. The *silver* salt forms colourless crystals, and the *calcium* salt can be obtained in two modifications. The *amide* melts at 195°; the *methylic* salt, a colourless oil of powerful odour, boils at 200—202°.

α-*Brom*-1 : 4-*ethylcyclopentanecarboxylic acid*,

$$CHEt \left\langle \begin{array}{c} CH_2 \cdot CBr \cdot COOH \\ CH_2 \cdot CH_2 \end{array} \right. ,$$
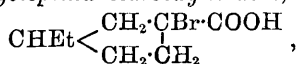
obtained by the application of Volhard's bromination process (Abstr., 1888, 129) to the foregoing acid, separates from hot formic acid in colourless, refractive needles which melt at 94°; when dissolved in soda, carbonic anhydride is evolved. The removal of 1 mol. HBr from this acid by means of hot quinoline, gives rise to Δ^1-1 : 4-ethyl-cyclopentenecarboxylic acid.

The dihydrobromide of paramethylenedihydrobenzoic acid has the constitution $CMe{<}^{CHBr \cdot CH_2}_{CH - CH_2}{>}CBr \cdot COOH$ (compare Abstr., 1893, i, 378), and, when reduced with zinc dust and glacial acetic acid, it gives rise to Δ^3-*tetrahydrotoluic acid*, which distils at 243—245°; this yields an *amide* melting at 117°. By the further reduction of this acid, a liquid hexahydroparatoluic acid is formed, the amide of which melts at 176—178°; it is, therefore, identical with the acid which Markovnikoff obtained by the reduction of paratoluic acid.

M. O. F.

Derivatives of Mandelic acid. By C. A. BISCHOFF and P. WALDEN (*Annalen*, **279**, 118—129) —When mandelic acid is heated at 200—205°, water and benzaldehyde distil leaving an amorphous mixture in the retort; similar results are obtained on heating the acid in a vacuum or in an atmosphere of carbonic anhydride. On distilling the acid in a current of air, or, preferably, under slightly reduced pressure, benzaldehyde, water, and diphenylmaleïc anhydride (Hintze, *Annalen*, **259**, 64) come over.

If mandelic acid is heated with phosphorus pentachloride at 100°, mandelic chloride is formed, and, on distillation, phenylchloracetic chloride is obtained; sodium phenylchloracetate yields only a small quantity of stilbene (?) on distillation. No dianhydride of the constitution $CHPh{<}^{CO \cdot O}_{O \cdot CO}{>}CHPh$ was obtained in any of the above reactions.

Mandelic anilide is easily prepared by heating the acid with aniline at 180—190°; it melts at 151—152°, not at 146° (compare Reissert and Kayser, Abstr., 1891, 438; Biedermann, Abstr., 1892, 473). If the mixture of acid and aniline is treated with phosphorus penta-chloride, *phenylchloracetanilide*, $CHPhCl \cdot CO \cdot NHPh$, is obtained; it crystallises in small, colourless needles, and melts at 151·5—152·5°. On reduction with sodium amalgam, it yields *phenylacetanilide*, $CH_2Ph \cdot CO \cdot NHPh$, which forms colourless leaflets melting at 116°, and may also be prepared by heating phenylacetic acid with aniline.

Mandelic orthotoluidide, $OH \cdot CHPh \cdot CO \cdot NH \cdot C_6H_4Me$, crystallises well, and melts at 72°; on treatment with phosphorus pentachloride, it yields *phenylchloracetorthotoluidide*, $CHPhCl \cdot CO \cdot NH \cdot C_6H_4Me$, which melts at 123—125°.

Mandelic paratoluidide melts at 172°, and *phenylchloracetoparatoluidide* at 142°; the latter, on reduction with sodium amalgam, yields *phenylacetoparatoluidide*, which melts at 132—133°.

Mandelic α-naphthalide, $CHPh(OH) \cdot CO \cdot NH \cdot C_{10}H_7$, forms colourless crystals melting at 140°, whilst the isomeric *β-naphthalide* crystallises in colourless, feathery leaflets melting at 189°. W. J. P.

Allocinnamic acid. By C. LIEBERMANN (*Ber.*, **27**, 2037—2051).
—Making use of J. Wislicenus' method of bromination of unsaturated acids (Abstr., 1893, i, 135), the author has improved the yield of methylic allocinnamate dibromide, and succeeded in isolating allocinnamic acid dibromide.

Allocinnamic acid dibromide melts at 91—93°, and differs from the stereoisomeric cinnamic dibromide in being readily soluble in cold carbon bisulphide and in benzene. It forms a clear solution with sodium hydroxide, and if excess of alkali is used, bromocinnamene is eliminated, identical with that obtained from the isomeric dibromide; this change also occurs on boiling with water. The allo-compound is less stable than cinnamic acid dibromide and its solution in sodium hydroxide, although not immediately decolorising potassium permanganate, produces this effect more rapidly than the isomeric modification.

Allocinnamic acid dichloride, which has not been obtained in a crystalline form, is prepared in an analogous manner by means of chlorine dissolved in carbon bisulphide. Like the preceding compound, it is accompanied by a considerable quantity of the cinnamic variety, cold carbon bisulphide affording, as in the previous case, an easy means of separation.

The *cinchonidine salt*, $C_{19}H_{22}N_2O,C_9H_8Br_2O_2$, has been the means of separating allocinnamic acid dibromide into its optically active constituents (compare Hirsch, this vol., i, 334). The maximum rotations obtained were $[\alpha]_D = +10°$ and $-71°$, but the former does not represent the optical activity of the pure dextro-acid, as this undergoes decomposition on boiling its solution in benzene, with formation of α-bromocinnamic acid. An attempt to prepare a racemic modification by mixing equal weights of cinnamic acid dibromide ($[\alpha]_D = +64°$) and allocinnamic acid dibromide ($[\alpha]_D = -70°$), dissolved in ether, led to a negative result.

Allocinnamic anhydride is prepared by boiling 8 parts of acetic anhydride with 5 parts of allocinnamic acid for 10 minutes. It forms a colourless oil, which, when heated or allowed to remain for some months in an exsiccator, is transformed into cinnamic anhydride.

Allocinnamylcocaïne is obtained from allocinnamylecgonine by saturating its solution in absolute methylic alcohol with hydrogen chloride; it occurs as an oil, and forms a *platinochloride*,

$$(C_{19}H_{23}NO_4)_2,H_2PtCl_6.$$
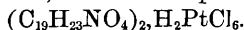
Allocinnamylcocaïne is decomposed by dilute acids with formation of ecgonine, methylic alcohol, and allocinnamic acid.

The crystallographic examination of allocinnamic acid has been reopened (compare Abstr., 1890, 1417); new forms have been observed, and results have been obtained which lead the author to conclude that this acid is identical with isocinnamic acid (Abstr., 1890, 494), although the description of the latter is too incomplete to confirm this opinion.   M. O. F.

Derivatives of Veratric acid and of Veratrol. By W. HEINISCH (*Monatsh.*, **15**, 229—234).—When dimethylprotocatechuic

acid (veratric acid), $C_6H_2(OMe)_2,COOH$, is treated with nitric acid, it is converted into nitrodimethylprotocatechuic acid and mono- and dinitrodimethylcatechol. The nitro-acid, separated from the product by extraction with dilute ammonia, melts at 187—188°.

When nitrodimethylprotocatechuic acid is reduced with the theoretical quantity of stannous chloride and hydrochloric acid, it is converted into amidodimethylcatechol, $C_6H_3(OMe)_2\cdot NH_2$. This crystallises in slender, yellow crystals, melts at 80°, and is identical with the compound obtained by the reduction of mononitrodimethylcatechol; the latter melts at 91°. The *platinochloride* is a crystalline, yellow precipitate, and melts at 208°.

Dinitrodimethylcatechol melts at 128·2—128·3°, and is identical with the compound obtained by nitrating dimethylcatechol (veratrol) and metahemipinic acid. When reduced with stannous chloride and hydrochloric acid, it is converted into *diamidodimethylcatechol*. The *hydrochloride* of the latter crystallises with 2HCl, but loses 1 mol. of hydrogen chloride on exposure to air.   E. C. R.

Dry Distillation of Calcium Diethylprotocatechuate. By W.
HEINISCH (*Monatsh.*, **15**, 235—238).—When dry calcium diethyl-protocatechuate (65 grams) is distilled, a brown, oily liquid (13 grams) is obtained, from which ethylic diethylprotocatechuate is dissolved on adding potassium hydroxide solution and shaking it with ether, whilst the alkaline solution contains ethylic diethylproto-catechuate. The latter crystallises in white needles, and melts at 163° ; monethylcatechol and a small quantity of a compound which the author believes to be diethylcatechol are also formed, and remain in the alkaline solution. The carbonaceous residue from the distillation contains catechol.

Monethylcatechol is a pale yellow oil, which boils at 240—241°, and with ferric chloride gives a green coloration, which quickly changes to brown, and is converted into a dirty violet by sodium carbonate.   E. C. R.

Dry Distillation of Calcium Trimethylgallate. By H.
ARNSTEIN (*Monatsh.*, **15**, 295—298).—Calcium trimethylgallate crystallises from water with $1\frac{1}{2}H_2O$. When subjected to dry distillation, it yields a dark brown oil which soon solidifies; if this is treated with ether and dilute sodium hydroxide, methylic trimethylgallate dissolves in the ether ; it melts at 81°, and on hydrolysis yields trimethylgallic acid (m. p. 167°). An oily residue was also obtained from the ethereal extract, and this, after boiling with potassium hydroxide, yields trimethylpyrogallol melting at 46°. The alkaline solution was found to contain a small quantity of dimethylpyrogallol ; it melts at 50°, and boils at 250°. No definite compound could be separated from the carbonaceous residue.   E. C. R.

Action of Ethylic Malonate on Benzylideneacetone. By D.
VORLÄNDER (*Ber.*, **27**, 2053—2058).—*Ethylic phenyldihydroresorcylate*, $C_{15}H_{16}O_4$, the sodium salt of which is formed when ethylic sodio-malonate acts on benzylideneacetone, is identical with the substance

obtained by Michael and Freer (Abstr., 1891, 914) on heating the additive product from ethylic sodacetoacetate with ethylic cinnamate. From the mode of formation, the formula $\begin{array}{c} CH_2 \cdot CO \cdot CH \cdot COOEt \\ | \quad\quad | \\ CO \cdot CH_2 \cdot CHPh \end{array}$ expresses its constitution, ethylic alcohol having been eliminated in the reaction. It crystallises from boiling water in colourless needles, which melt at 143°; the aqueous solution has an acid reaction, and the substance is readily soluble in caustic alkalis and alkali carbonates. It forms a colourless, unstable, silver salt, and its solution in alcohol is coloured brown by ferric chloride. Phenylhydrazine and hydroxylamine give rise to amorphous derivatives.

Phenyldihydroresorcylic acid, $C_{13}H_{12}O_4$, is obtained by the hydrolysis of the ethylic salt. It melts at 98°, losing carbonic anhydride with formation of *phenyldihydroresorcinol*, $C_{12}H_{12}O_2$, which is most conveniently prepared by boiling ethylic phenyldihydroresorcylate for several hours with aqueous sodium carbonate. It forms colourless plates, which become red at 150°, and melts at 184°, decomposing with evolution of gas; the alcoholic solution becomes reddish-brown on the addition of ferric chloride. When distilled with zinc-dust, diphenyl is liberated, the hydrocarbon being easily recognised by its odour. The *dioxime* melts at 177°; it is insoluble in sodium carbonate, but dissolves in caustic alkalis, reducing Fehling's solution on warming.

β-Phenyl-γ-acetobutyric acid, $C_{12}H_{14}O_3$, may be obtained either from ethylic phenyldihydroresorcylate by the prolonged action of hydrochloric acid, or by boiling phenyldihydroresorcinol with acids or alkalis; it forms long prisms, which melt at 83°.

Other unsaturated ketones also react with ethylic malonate, two molecular proportions of which unite with dibenzylideneacetone. The presence of an acetyl-group facilitates the elimination of alcohol from the additive products, and in the case of the compound from benzylideneacetophenone, no intramolecular condensation takes place.

It is found that ethylic cyanacetate may be substituted for ethylic malonate in this action. Thus, from benzylideneacetone, the *nitrile* of phenyldihydroresorcylic acid, $C_{12}H_{11}O_2 \cdot CN$, is obtained, crystallising in prisms which melt at 175°; a brown coloration is developed with ferric chloride.

In the case of ethylic acetoacetate, the action proceeds somewhat differently, 1 mol. of water being eliminated, with formation of a *substance* having the formula $C_{16}H_{18}O_3$; this melts at 94°, and gives a green coloration with ferric chloride.   M. O. F.

Alkylhaloïds of Quinic acid. By F. Stohr (*Chem. Centr.*, 1894, i, 428; from *Pharm. Post*, **27**, 13).—*Quinic acid methiodide* forms a pale, reddish-brown precipitate, which becomes yellow when dried and powdered; it melts and decomposes at 250°. The *methochloride* yields golden-yellow needles melting at 215°. By treatment with silver nitrate or sulphate, the iodide yields the *methonitrate* and *methosulphate*. The *ethobromide* and *propobromide*, and some alkylbetaïnes of quinic acid, are also described.   L. T. T.

Orthamidodiphenyl from Fluorene. By C. GRAEBE and A. S. RATEANU (*Annalen*, **279**, 257—267).—The preparation of orthamido-diphenyl, either by nitrating diphenyl and reducing the nitro-compound, or by heating aniline with diazoamidobenzene, is not convenient, because the product consists in both cases chiefly of the para-compound. It may be much more advantageously obtained from fluorene; this is first converted into diphenylene ketone by oxidation with acetic acid and sodium dichromate, and the ketone is then fused with potash at about 180—200°, the temperature not being allowed to rise above the latter limit; in this way, it is converted into diphenylortho-carboxylic acid, which boils at 343—344° (corr.). When this acid is treated with phosphorus pentachloride, the chloride is formed, but cannot be obtained pure, as it begins to decompose at 60—70°, with loss of hydrogen chloride, diphenylene ketone being regenerated. The crude mixture of the chloride with phosphorus oxychloride may, however, be utilised for the preparation of the amide of the acid by diluting it with benzene, and passing ammonia into the cooled solution. The amide may also be prepared, the yield being about the same as in the process just described, by heating the sodium salt of diphenylorthocarboxylic acid with ammonium thiocyanate. Di-phenylorthocarboxyamide, $C_6H_4Ph\cdot CONH_2$, crystallises in colourless needles, melts at 177°, and may be distilled without decomposing. It is only slowly attacked by alcoholic potash, and is scarcely altered by aqueous potash at 160—170°. Finally, orthamidodiphenyl is obtained by treating the amide with sodium hypobromite solution in the usual way. It boils at 299°. Special attention was paid throughout the series of preparations to the yields obtained, which were as follows:—100 grams of fluorene yielded 90 grams of diphenylene ketone, 80 grams of diphenylorthocarboxylic acid, 65 grams of di-phenylorthocarboxyamide, 50 grams of orthamidodiphenyl.

The following observations were also made during the course of the research. Ethylic diphenylorthocarboxylate boils at 314° (Schmitz, 300—305°), whilst the *methylic* salt boils at 308°. The *anilide of diphenylorthocarboxylic acid* may readily be obtained by heating the acid with aniline; it crystallises in large prisms melting at 100°.

Orthoacetylamidodiphenyl crystallises from alcohol in colourless prisms melting at 117·5°. *Diphenyl-hydrazine*, $C_{12}H_9\cdot NH\cdot NH_2$, is prepared by diazotising amidodiphenyl and reducing the diazo-compound with stannous chloride and hydrochloric acid; it forms prismatic crystals, melts at 38°, readily reduces Fehling's solution, and forms condensation products with aldehyde and acetone. The *hydrochloride* separates from water in colourless crystals.　　　　　　　A. H.

The Methylacridones and Methylacridines. By C. GRAEBE (*Annalen*, **279**, 268—270).—Introductory remarks to the next three abstracts. The derivatives to be described were prepared by the methods previously employed by Graebe and Lagodzinski (Abstr., 1893, i, 649).　　　　　　　　　　　　　　　A. H.

2-Methylacridone and 2-Methylacridine. By S. KAHN (*Annalen*, **279**, 270—275; compare the foregoing abstract).—*Nitropara-*

tolylanthranilic acid, $C_7H_7\cdot NH\cdot C_6H_3(NO_2)\cdot COOH$ [= 6 : 3 : 1], is obtained by heating orthochloronitrobenzoic acid [1 : 6 : 3] with paratoluidine. It crystallises from glacial acetic acid in yellow needles, which melt at 262·5° (corr.). The *potassium* salt, $C_{14}H_{11}N_2O_4K +$ $2\frac{1}{2}H_2O$, forms yellow needles, and the *barium* salt, $(C_{14}H_{11}N_2O_4)_2Ba +$ $7H_2O$, vermilion coloured crystals. *Amidoparatolylanthranilic acid* separates from alcohol in colourless prisms which readily become coloured; it melts at 220° (corr.). The *hydrochloride* is partially decomposed by boiling water.

Paratolylanthranilic acid, $C_7H_7\cdot NH\cdot C_6H_4\cdot COOH$, forms colourless needles melting at 191·5° (corr.); it is soluble in concentrated hydrochloric acid, but is reprecipitated on adding water. The *barium* salt is only slightly soluble in hot water.

2-Methylacridone, $C_6H_4{<}_{NH}^{CO}{>}C_6H_3Me$, is formed when paratolylanthranilic acid is heated on the water-bath with sulphuric acid. It crystallises from alcohol in yellow prisms, melts at 338° (corr.), and is insoluble in aqueous alkalis; its solution in alcohol has an intense blue fluorescence. When it is heated with zinc dust, 2-methyl-acridine, $C_6H_4{<}_{N}^{CH}{>}C_6H_3Me$, is formed; this substance has previously been prepared by Bonna (Abstr., 1887, 927) from phenyl-paratoluidine, and by Ullmann (*J. pr. Chem.*, **36**, 265) from di-amidodimethyltriphenylmethane. When pure, it melts at 134° (corr.); the *chromate*, $(C_{14}H_{11}N)_2H_2Cr_2O_7$, forms yellow prisms, and the *platinochloride* is a yellow, sparingly soluble salt. When methyl-acridine is treated with sodium amalgam, it is converted into *2-methylhydroacridine*, $C_6H_4{<}_{NH}^{CH_2}{>}C_6H_3Me$, which crystallises in colourless plates, melts at 157° (corr.), and does not combine with acids. It is readily reconverted into methylacridine by oxidation with chromic acid.   A. H.

4-Methylacridone and 4-Methylacridine. By J. LOCHER (*Annalen*, **279**, 275—280; compare the two preceding abstracts).— *Nitrorthotolylanthranilic acid*, [COOH : NH : NO₂ = 1 : 2 : 5], crystallises from alcohol in slender, pale yellow needles melting at 253—254°, and is almost insoluble in water. The *sodium* salt crystallises with $3H_2O$, the *potassium* salt with $2H_2O$, whilst the *silver* salt is a brownish-red powder. *Amidorthotolylanthranilic acid* decomposes when heated above 200°, and forms salts with bases and with strong acids. The *hydrochloride* crystallises in colourless plates, and is decomposed when boiled with a large quantity of water. *Orthotolylanthranilic acid* forms colourless crystals melting at 179°, and is sparingly soluble in hot hydrochloric acid. The *silver* salt is a white powder. *4-Methylacridone* crystallises from alcohol in greenish-yellow needles, melts at 345—346° (corr.), and may be sublimed in needles. It is readily soluble in hot alcohol, forming a solution which has an intense blue fluorescence.

Dimethylacridone, $C_6H_4{<}{CO-\atop NMe}{>}C_6H_3Me$, is obtained by the action
of methylic iodide and potash on 4-methylacridone, and forms greenish-yellow needles melting at 183—184°. Alcohol dissolves it freely, forming a solution with an intense blue fluorescence.

4-Methylacridine crystallises in needles, melts at 88°, and may be distilled; its vapour attacks the mucous membrane. It dissolves sparingly in hot water, readily in alcohol, and the solutions as well as the solid act on the skin. The salts are yellow, and their solutions exhibit an intense blue fluorescence. The *dichromate* forms yellow needles, and the *picrate* slender, yellow needles, which are insoluble in alcohol. On oxidation with chromic acid, it yields a mixture of acridone and diacridonyl melting at 250°. A. H.

2 : 4-Dimethylacridone and 2 : 4-Dimethylacridine. By V. KAUFMANN (*Annalen*, **279**, 281—288; compare the three preceding abstracts).—*Nitro-xylylanthranilic acid*,

$$COOH·C_6H_3(NO_2)·NH·C_6H_3Me_2,$$
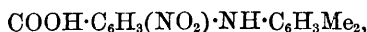
is obtained by heating metanitrorthochlorobenzoic acid with 1 : 3 : 4-xylidine. It crystallises from alcohol in yellow needles, and melts and slightly decomposes at 241°. The *potassium* salt crystallises with $1H_2O$, the *barium* salt with $5H_2O$. *Amido-xylylanthranilic acid*, prepared by reducing the nitro-compound with ferrous sulphate and ammonia, crystallises in colourless, microscopic needles, which readily become dark coloured on exposure to air; it melts and slightly decomposes at about 242°. The *hydrochloride* forms yellow needles which are only sparingly soluble in cold water. *Benzamido-xylylanthranilic acid* is a yellow powder which melts at 264—265°, and is moderately soluble in alcohol. *Xylyanthranilic acid* crystallises in colourless needles which rapidly become coloured in the air; it melts at 182°. The *silver* salt is a white powder sparingly soluble in alcohol.

2 : 4-Dimethylacridone, $C_6H_4{<}{C\ O\atop NH}{>}C_6H_2Me_2$, is obtained by sublimation in sulphur-yellow needles, melting at 294°; it is insoluble in aqueous alkalis, but forms a blue fluorescent solution in alcohol. *2 : 4-Dimethylacridine* melts at 71°; it has the characteristic acridine odour, but its vapour does not attack the mucous membrane so violently as that of acridine, whilst the solid substance does not appear to act on the skin. The *hydrochloride* is soluble in hydrochloric acid; the *platinochloride* and *picrate* form yellow crystals.

2 : 4-Dimethylchloracridine, $C_6H_4{<}{CCl\atop N—}{>}C_6H_2Me_2$, is obtained by heating dimethylacridone with phosphorus pentachloride. It crystallises in colourless needles, melts at 108°, and is converted into dimethylacridone by boiling with alcohol or water. The *platinochloride* is only sparingly soluble in water. *Dihydrodimethylacridine*, $C_6H_4{<}{CH_2\atop NH}{>}C_6H_2Me_2$, which crystallises in colourless plates, melting

2 *p* 2

at 80°, is formed, along with an insoluble substance, which melts at 155—156°, when dimethylacridine or dimethylacridone is treated in alcoholic solution with sodium amalgam.   A. H.

Ethereal Salts of Natural Naphthenic acids. By. V. MARKOVNIKOFF (*J. Russ. Chem. Soc.*, **25**, 654—658).—The methyl salts of the lower natural naphthenic acids were prepared and fractionated with a view to isolate the methyl salt of heptanaphthenic acid (hexahydrobenzoic acid). This salt boils at 181—183°, and the fraction boiling at 180—182° gave numbers, on analysis, not far removed from those required by the formula, a slight excess of hydrogen being attributed by the author to the presence of fatty acids along with the naphthenic acids.   J. W.

Hydroxynaphthaquinoneimidobenzoic acid. By D. A. CHARDIN (*J. Russ. Chem. Soc.*, **25**, 685—687).—Orthoamidobenzoic acid condenses very readily with β-naphthaquinone, giving β-hydroxynaphthaquinoneamidobenzoic acid, $OH \cdot C_{10}H_5O \colon N \cdot C_6H_4 \cdot COOH$, which crystallises in bronze-red scales, and melts at 270—271°. It can be heated to 180° with sulphuric acid without undergoing decomposition. On long-continued boiling with hydrochloric acid, it yields hydroxynaphthaquinone and amidobenzoic acid. On reduction, it yields a colourless substance which oxidises to the original compound if exposed to the air.   J. W.

Synthesis of α-Alkyl-β-naphthocinchonic acids: Specific Reaction for Aldehydes. By O. DOEBNER (*Ber.*, **27**, 2020—2030; compare this vol., i, 261).—The action which takes place when an aldehyde is heated with pyruvic acid and β-naphthylamine dissolved in alcohol has been applied to all classes of aldehydes, and is found to take effect in every case except that of hydroxyaldehydes such as glycerose, in which an hydroxyl group is linked to the carbon atom to which the aldehydic residue is attached. The author regards this circumstance as explaining the fact that the test does not apply to those sugars which are represented as aldehydes.

β-Naphthocinchonic acids have been prepared from the following aldehydes :—Acetaldehyde, propaldehyde, isobutaldehyde, isovaleraldehyde, œnanthaldehyde, crotonaldehyde, tiglic aldehyde, citronellic aldehyde, citral, aldol, furfuraldehyde, salicylaldehyde, anisaldehyde, vanillin, piperonal, and cuminaldehyde. On heating the several naphthocinchonic acids above their melting points, the corresponding α-alkyl-β-naphthoquinolines are formed.

The α-alkyl-β-naphthocinchonic acids possess the salt-forming properties both of acid and of base, yielding not only metallic salts, but also hydrochlorides and platinochlorides.   M. O. F.

Hydroxyanthraquinones. By H. OFFERMANN (*Annalen*, **280**, 1—35).—It has long been known that when the condensation of metahydroxybenzoic acid is effected by means of sulphuric acid

diluted with 10 per cent. of water, 1 : 4'-, 2 : 3'- and 2 : 1'-dihydroxy-anthraquinones are formed. Employing concentrated acid, the author has obtained exclusively a sulphonic acid which is split up into anthraflavic and sulphuric acids when heated in a closed tube with hydrochloric acid, and which yields flavopurpurin when fused with potash, showing it to be 1 : 2 : 3'-dihydroxyanthraquinonesulph-onic acid or sulphoanthraflavic acid; when this acid is heated with hydrochloric and dilute sulphuric acids at 250°, metahydroxybenzoic acid is formed, together with a small quantity of anthraflavic acid.

Studying the action of fused potash on 1 : 4'- and 1 : 3'-anthra-quinonedisulphonic acids, Dehnst observed that the intermediate products, anthrarufin and chrysazin, undergo a change of a two-fold character, hydroxybenzoic acids being formed, accompanied on the other hand by hydroxychrysazin. It is found that whilst anthra-flavic acid under similar treatment does not give rise to definite pro-ducts, 1 : 2'-dihydroxyanthraquinone when fused with a mixture of caustic soda and potash yields, according to temperature, either anthrapurpurin or an isomeric trihydroxyanthraquinone (compare Dehnst, *Ber.*, **12**, 1293). The latter compound is obtained when the temperature of the mixture is gradually raised from 190° to 300°, and forms small red needles, the properties of which correspond in all respects with those described by Dehnst (*loc. cit.*) ; the *acetyl* deriva-tive, $C_{14}H_5O_2(OAc)_3$, crystallises from glacial acetic acid in hexagonal plates which melt at 205°.

Although hydroxybenzoic acids are not formed by fusing anthra-flavic acid and 1 : 2'-dihydroxyanthraquinone with potash, this de-composition is effected when the anthraquinonedisulphonic acids, from which these compounds are derived, are made the starting point of the reaction. Treated in this way, 2 : 3'-anthraquinonedisulphonic acid yields protocatechuic acid, meta- and parahydroxybenzoic acids, and most probably 1 : 2 : 3-dihydroxybenzoic acid. Contrary to the statement of Hlasiwetz and Barth (*Annalen*, **134**, 276), the first-named of these may be easily separated from parahydroxybenzoic acid, the basic lead salt of which is soluble in water. In like manner, 2 : 2'-anthraquinonedisulphonic acid yields anthrapurpurin, which at a higher temperature becomes converted into the above-mentioned isomeride, together with protocatechuic and metahydroxybenzoic acids, unaccompanied, however, by parahydroxybenzoic acid.

The paper concludes with the theoretical consideration of these results and their significance in determining the constitution of poly-hydroxyanthraquinones. M. O. F.

Constitution of Euxanthone. By S. v. KOSTANECKI (*Ber.*, **27**, 1989—1993).—From Graebe's investigations, the hydroxyl groups in euxanthone appear to occupy the positions 3—4', the author's syn-thesis indicates the constitution 5—4'. The *methyl-5-hydroxyxanth-ones*, formed by the action of resorcinol on the three commercial hydroxytoluic acids in presence of acetic anhydride, are purified by means of their crystalline *sodium salts*, from the methyl-3-hydroxy-xanthones, which are formed in very small quantity, and from the dimethylxanthones. *2' : 5-Methylhydroxyxanthone* crystallises in

yellow needles melting at 152°. 3' : 5-*Methylhydroxyxanthone* and
4' : 5-*methylhydroxyxanthone* are deposited in yellow plates, and melt
at 176° and 135° respectively. 1 : 3 : 5-Methyldihydroxybenzene and
1 : 2 : 4-methyldihydroxybenzene combine with salicylic acid to form
methyl-5-hydroxyxanthones, the yield of methyl-3-hydroxyxanthones
is extremely small. 4 : 5- or 2 : 5-*Methylhydroxyxanthone* crystallises
in yellow needles melting at 112°. 1 : 3 : 5-Methyldihydroxybenzene
combines with the hydroxytoluic acids to form the following :
2' : 3 : 5-*dimethylhydroxyxanthone*, 3' : 3 : 5-*dimethylhydroxyxanthone*,
and 4' : 3 : 5-*dimethylhydroxyxanthone* ; these crystallise in yellow
needles, and melt at 145°, 139°, and 169° respectively. Dimethyl-3-
hydroxy-derivatives were formed in very small quantity only. In all
these cases, the acid radicle attacks the phenol between the hydroxyl
groups, therefore isoeuxanthone, from resorcinol and 2 : 4-dihydroxy-
benzoic acid, should be either 3 : 3'- or 5 : 3'-dihydroxyxanthone ;
that the latter formula is correct is shown by the production of a
monomethyl ether, which crystallises in yellow plates, melts at
143—144°, yields a crystalline *sodium salt*, and an *acetyl derivative*,
crystallising in colourless plates, and melting at 150°.

Euxanthone methyl ether, $OMe\cdot C_{13}H_6O_2\cdot OH$ [OMe : OH = 4' : 5], is
prepared in a similar manner, and crystallises in yellow plates melt-
ing at 129°. The *sodium salt* is crystalline, and insoluble in alkalis.

Attempts to prepare 2 : 4 : 5 : 4'-dimethyldihydroxyxanthone from
2 : 5-dihydroxybenzoic acid and 1 : 3 : 4 : 6-dimethyldihydroxybenzene
were not very successful, only a small quantity of a compound
was formed, which gave the characteristic euxanthone reaction with
sodium amalgam. 1 : 3 : 5-Methyldihydroxybenzene and 2 : 5-di-
hydroxybenzoic acid, in presence of zinc chloride, combine to form
3' : 5 : 4'-*methyldihydroxyxanthone*, which crystallises, and sublimes
in long, yellow needles, melts at 252°, and resembles euxanthone in
its behaviour towards sodium amalgam. The *diacetyl-derivative* crys-
tallises in small, colourless needles melting at 163°.   J. B. T.

Hydroxyxanthone Derivatives and Maclurin. By E. König
and S. v. Kostanecki (*Ber.*, **27**, 1994—1997).—The following brom-
hydroxyxanthones were prepared by the action of bromine on the
hydroxyxanthone in glacial acetic acid solution, for the sake of compar-
ing them with the corresponding derivatives of yellow vegetable colour-
ing matters. *Dibromo-5-hydroxyxanthone* crystallises in long, yellow,
lustrous needles melting at 222°. *Dibromo-4-hydroxyxanthone* forms
pale yellow needles melting at 207°. The *sodium salt* is intensely
yellow. *Dibromo-3-hydroxyxanthone* crystallises in long, colourless
needles, and melts at 269—272° ; the *sodium salt* is also colourless.
Dibromo-2-hydroxyxanthone is deposited in colourless needles ; it melts
at 274—276°, and dissolves in alkalis with a yellow colour. *Dibromo-*
5 : 3-*dihydroxyxanthone* forms pale yellow needles melting at 245°.
Dibromo-5 : 4'-dihydroxyxanthone (euxanthone) crystallises in yellow
needles, and melts at 280°. *Dibromo-5 : 4'-hydroxymethoxyxanthone*
crystallises in yellow needles, melts at 196°, and is also formed by the
action of methylic iodide and potassium hydroxide on the preceding
compound. The *sodium salt* is yellow, and insoluble. *Tetrabromo-*

5 : 3′-*dihydroxyxanthone* (isoeuxanthone) was only obtained in small quantity; it crystallises in pale yellow needles, and melts at 280°. The following four benzoyl derivatives crystallise in colourless needles: *benzoyl-5-hydroxyxanthone*, melting at 206·5°; *benzoyl-4-hydroxyxanthone*, melting at 151°; *benzoyl-3-hydroxyxanthone*, melting at 147°; *benzoyl-2-hydroxyxanthone*, melting at 172°.

Maclurin, which is readily resolved into phloroglucinol and 3 : 4-dihydroxybenzoic acid, also appears to be a hydroxyketone ; it yields a *pentabenzoyl-derivative*, which forms colourless, glittering crystals melting at 153—156°.   J. B. T.

Orientation in the Terpene Series: the Terpenones of the Carvone Group. By A. BAEYER (*Ber.*, **27**, 1915—1923; compare this vol., i, 92, 252, 297).—Dihydrocarvone unites with hydrogen bromide in acetic acid solution, forming an additive compound, which, on treatment with alkalis, loses hydrogen bromide, yielding an isomeride of dihydrocarvone, to which the name *carone* has been given. It is a colourless oil, having an odour resembling that of camphor and peppermint, and boils at about 210°, undergoing slight decomposition. Its *oxime* is liquid, but with semicarbazide it yields a crystalline derivative, $C_{10}H_{16}$:N·NH·CO·NH$_2$, which forms acute needles or long prisms, and melts at 169°. Another crystalline derivative, obtained by the action of amidoguanidine picrate, separates from alcohol in concentric groups of prisms or flat plates. Carone is very stable towards potassium permanganate, and is only very slowly attacked by bromine; it differs, therefore, from other compounds hitherto obtained by the action of alkalis on brominated hydrobenzene-derivatives, which have, one and all, shown reactions consistent with the supposition that they contain an ethylene linking. The above formation of carone renders untenable the author's previous supposition that compounds containing ethylene linkings were invariably formed under these circumstances. The most probable supposition as to the constitution of carone is that it contains a para-linking, its constitution being analogous to that proposed by Semmler for tanacetone (this vol., i, 339). The most probable formulæ for dihydrocarvone, its hydrobromide, and carone are as follows.
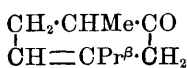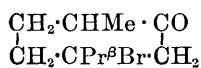
$$CH_2 \cdot CHMe \cdot CO \qquad CH_2 \cdot CHMe \cdot CO \qquad CH_2 \cdot CMe \cdot CO$$
$$CH = CPr^\beta \cdot CH_2 \qquad CH_2 \cdot CPr^\beta Br \cdot CH_2 \qquad CH_2 \cdot CPr^\beta \cdot CH_2$$
Dihydrocarvone.   Hydrobromide.   Carone.
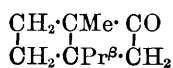
The compound obtained by the action of bromine on carone has not been obtained crystalline, but, as no hydrogen bromide is evolved, it must be an additive compound. If the above formula is correct, it must be the ketone of dipentene dihydrobromide ; experiments to ascertain whether this is so are now in progress. Hydrobromic acid converts carone into the hydrobromide from which it was prepared.

When dihydrocarvone is treated with sulphuric acid at 0°, it is converted into the compound termed *carveol* by the author, and already obtained by Wallach (this vol., i, 44), by heating the oxidation pro-

duct of solid terpineol with dilute sulphuric acid; carone, likewise, yields the same compound on heating, so that carveol appears to be the final product of intramolecular change of several members of this series. The same series of reactions which is employed for the conversion of carvone into isocarvoxime, brings about the conversion of dihydrocarvone into carveol. For this purpose, dihydrocarvoxime is treated with hydrogen bromide in acetic acid solution, and the product subjected to the action of potash in methylic alcohol solution, carveoloxime being thus obtained.

Eucarvone, on reduction with sodium in alcoholic solution, yields the corresponding *dihydroeucarveol*, $C_{10}H_{18}O$, which has a camphor-like odour, boils at 109—110°, under a pressure of 21 mm., and is still an unsaturated compound. When oxidised with chromic acid, it yields a ketone, having the composition of a terpenone, termed *dihydroeucarvone*, $C_{10}H_{16}O$; this has a faint odour of peppermint and camphor, boils at 86—88°, under 14 mm. pressure, and yields an oily oxime. The latter forms a crystalline *hydriodide*, which may be obtained in colourless prisms; it melts at 161°, and is only slightly soluble in the ordinary solvents. The *semicarbazide compound* crystallises in plates, and melts at 189—191°. Dihydroeucarvone also readily yields a crystalline *nitroso-compound*, which forms large prisms, melts and decomposes at 119—120°, and is probably a tertiary derivative similar to that of menthone (this vol., i, 522).

Semicarbazide may in many cases be employed with advantage in the isolation of ketones, as the derivatives are often crystalline when the oximes and hydrazones are oils. The semicarbazide compounds are also very readily resolved into their components by the action of dilute acids. In cases where the semicarbazide does not give good results, amidoguanidine may be employed, the product being isolated as the picrate.

The following table gives the melting points and crystalline forms of the semicarbazide compounds of the carvone group.

	Melting-point.	Crystalline form.
Tanacetone.	171—172°	Acute prisms.
Carone	167—169	Long needles and prisms.
Dihydrocarvone. .	187—188	Slender prisms with blunt ends.
Dihydroeucarvone	189—191	Thin plates.
Carveol	202—205	Spindles or six-sided plates.
Carvotanacetone .	177—179	Rhombic tablets and oblique prism.
Carvone	162—163	Six-sided plates.
Eucarvone	183—185	Concentric aggregates of prisms.

H. G. C.

The Carvone Series. By O. WALLACH and H. SCHRADER (*Annalen*, **279**, 366—390).—In the preparation of carvoxime, for which an excess of hydroxylamine has to be employed, a *compound*, of the formula $C_{10}H_{14}:NOH,NH_2 \cdot OH$, is obtained as a thick syrup, which crystallises very slowly, and then melts at 174—175°.

When carvoxime is dissolved in sulphuric acid, it undergoes molecular change, and is converted into *paramidothymol*,

$$OH \cdot C \underset{CPr:CH}{\overset{CH \cdot CMe}{<}} \!\!\!\!> C \cdot NH_2,$$
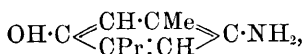
which melts at 173—174°. The constitution of this substance is proved by the facts that when its diazo-salts are boiled with water, thymoquinone is formed, whilst with alcohol, thymol itself is produced. It is probable that the carvoxime, $HC \underset{CPr \underline{\hspace{2mm}} CH}{\overset{CH \cdot CHMe}{<}} \!\!\!\!> C:NOH$, first passes into the form of cymylhydroxylamine,

$$HC \underset{CPr:CH}{\overset{CH \cdot CMe}{<}} \!\!\!\!> C \cdot NH \cdot OH,$$
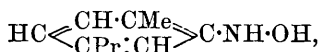
which is then converted by the action of the acid into amidothymol.

When carvoxime is heated with strong aqueous potash at 230—240°, carvacrylamine, $C_{10}H_{15}N$, is obtained. This substance, when treated with acetic anhydride, is converted into a *diacetyl*-derivative, which melts at 66°. The conversion of the carvoxime into this base proceeds at a lower temperature in the presence of stannous chloride, and is probably due to the action of the potash on the cymylhydroxylamine, into which the oxime may be supposed to pass.

Reduction of Carvone.—When carvone is reduced by means of alcohol and sodium, dihydrocarveol is formed, whilst if dilute potash or acetic acid and zinc dust are used, dihydrocarvone, identical with the substance obtained by the oxidation of dihydrocarveol, is formed. In addition to this ketone, a substance of the empirical formula, $C_{10}H_{15}O$, is produced, which is probably the *pinacone* of the series; it crystallises in large prisms, which have a vitreous lustre and melt at 148—149°. Both the pinacone and dihydrocarvone derived from *d*-carvone are lævorotatory. Dihydrocarvoxime (Abstr., 1893, i, 595) crystallises in two forms, sparingly soluble needles and transparent prisms, melting at 88—89°. When left in contact with alcohol, the needles gradually become converted into prisms. When the oxime is treated with sulphuric acid, it is converted into *isocarvoxime*, which melts at 87—88°, crystallises only in prisms, and is much more stable towards hot dilute sulphuric acid than the true oxime. Dihydrocarvoxime (*d*- or *l*-) readily combines with hydrogen bromide in acetic acid solution, forming *bromotetrahydrocarvoxime*, $C_{10}H_{17}Br:N \cdot OH$, which crystallises well from ether, and melts and decomposes at 109°. Both forms of the true oxime yield this compound, whilst the iso-oxime does not unite with hydrogen bromide under these conditions. When this hydrobromide is melted, it loses water and is converted into the hydrobromide of carvacrylamine; this reaction indicates the close relation which exists between the isomeric compounds, dihydrocarvone and thujone (Abstr., 1893, i, 107).

The fraction of thuja oil, boiling at 220—230°, contains a hydrocarvone, which yields an oxime melting at 93—94°, and easily forms a compound with hydrogen sulphide melting at about 94—95°. It is possible that this substance is identical with the carvo-tanacetone obtained by Semmler (this vol., i, 339). The isomeride of

dihydrocarvone, obtained by oxidising dihydrocarveol (this vol., i, 45), reacts with hydroxylamine, giving a mixture of two isomeric substances, one of which melts at 111—112°, whilst the other melts at 164—165°; the nature of the latter has not yet been decided.

The ketone previously described (this vol., i, 45), as prepared indirectly from pinylamine, may be known as *isocarvone;* it boils at 222—224°, has a sp. gr. of 0·989 at 19°, and a specific refractive index $n_D = 1·5067$. It is therefore of the same degree of saturation as carvone, and, like it, combines with hydrogen sulphide.

The characterisation of the carvones and hydrocarvones by means of their oximes is very unsatisfactory, as these substances resemble one another in melting point, &c., very closely. The bromides have not hitherto been obtained crystalline, but may be prepared in this state by dissolving the substance in an acetic acid solution of hydrogen bromide, and adding bromine. Dihydrocarvone, treated in this way, yields the *dibromide,* $C_{10}H_{16}O,Br_2$, in lustrous crystals. The active modifications of this bromide melt at 69—70°, whilst the racemic modification melts at 96—97°. *Carvone tetrabromide,* $C_{10}H_{14}O,Br_4$, may be prepared in a similar manner. The active compound melts at 119—121°, the racemic at 74—76°. A. H.

Sesquiterpenes. By O. WALLACH and F. E. TUTTLE *(Annalen,* **279**, 391—397; compare Abstr., 1893, i, 101).—*Caryophyllen nitrosate,* $C_{15}H_{24}·N_2O_4$, crystallises from benzene in slender needles melting at 148—149°. With piperidine, it yields a *nitrolamine,*

$$C_{15}H_{24}(NO)·NC_5H_{11},$$
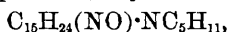
which forms transparent crystals melting at 141—143°. The *urethane of caryophyllen alcohol,* $NHPh·COOC_{15}H_{25}$, crystallises in needles melting at 136—137°. The *acetate,* $C_{15}H_{25}·OAc$, may be prepared by digesting the iodide with sodium acetate and acetic acid. The previously described hydrocarbon, $C_{30}H_{50}$, when pure, crystallises in large prisms, and melts at 144—145°.

Patchouli alcohol, $C_{15}H_{25}·OH$, is converted by even the feeblest dehydrating agents into *patchoulene,* $C_{15}H_{24}$, which boils at 254—256°; its sp. gr. at 23° is 0·939, and its refractive index $n_D = 1·50094$, so that it only contains one ethylene linking. The alcohol is probably tertiary.

The substance known commercially as champacol, obtained from Champaca wood by distillation with steam, is identical with a product previously obtained from guaia-wood. The pure compound, which may be called *guaiol,* melts at 91°, boils at 288°, and is an alcohol. It is not altered by dilute sulphuric acid, and gives a deep red coloration with phosphoric anhydride. When heated with zinc chloride, and then distilled in steam, a blue oil passes over. This has the formula $C_{15}H_{24}$, and boils at 124—128°; its sp. gr. at 20° is 0·910, and its refractive index $n_D = 1·50114$. The origin of the blue colour has not yet been ascertained. A. H.

Isomeric Camphoric acids. By O. ASCHAN *(Ber.,* **27**, 2001—2012).—Thirteen modifications of camphoric acid have been described at various times, namely :—(1), ordinary dextrocamphoric acid;

(2), Chautard's lævocamphoric acid; (3), Chautard's paracamphoric acid, the racemic compound of Nos. 1 and 2; (4), Chautard's inactive camphoric acid from diethylic paracamphorate (No. 3); (5), Wreden's mesocamphoric acid, which is apparently inactive; (6), Wreden's i-camphoric acid (m. p. 160°); (7), Armstrong and Tilden's i-camphoric acid (m. p. 202°); (8), Jungfleisch's i-camphoric acid formed by the action of water at 280° on No. 1; (9), lævoisocamphoric acid; (10), Jungfleisch's i(?)-acid formed by the action of water on No. 2, and corresponding with No. 5; (11), Jungfleisch's dextroisocamphoric acid; (12), i-camphoric acid, the racemic compound of Nos. 9 and 11; (13), Marsh and Stockdale's i-camphoric acid.   On comparison, it is found that only six of these, that is Nos. 1, 2, 3, 9, 11, and 12, are definite compounds; the remainder are either identical with one of these six, or are mixtures of varying composition.   The three camphoric acids, Nos. 1, 2, and 3, are sharply differentiated from the three isocamphoric acids by the ease with which they form anhydrides, they have, therefore, the maleïnoïd or cis configuration, the isocamphoric acids having the fumaroïd or cistrans configuration.   In both series, the two active acids are identical in chemical and physical properties, with the exception of the optical activity, which is equal and opposite; the active camphoric acids melt at 187°; the active isocamphoric acids at 171—172°. i-Camphoric acid melts at 202—203°; i-isocamphoric acid at 191°; both are less soluble than the active acids from which they are formed and into which they are not resolved by crystallisation; they are optically inactive.   Mixtures of equal parts of an acid from each series with opposite activities (mesocamphoric acids) have variable melting points much below those of their components, they have a feeble optical activity, and are resolved into their constituents by fractional crystallisation, and quantitatively by the action of acetic chloride, which readily converts the camphoric acids into anhydrides, but is without action on the isocamphoric acids.   The conversion of an active acid of one series into that of another (cis into cistrans or *vice versâ*) by the action of water at high temperatures only proceeds to the extent of about 50 per cent., and the acid produced has the opposite sign of activity to that of the original one; all attempts, however, to convert an active acid into the racemic form, or into its complementary active modification of the same series, have been unsuccessful.   The reaction takes place more quickly at a lower temperature, and the yield is increased, by the use of a mixture of glacial acetic acid and concentrated hydrochloric acid instead of water.   The isocamphoric acids may also be converted into camphoric acids, with opposite activities, by dry distillation, anhydrides being first formed, but the inverse change (cis into cistrans) does not take place.   The same change, which applies to each series, is produced by the action of bromine on the acid and the subsequent reduction of the brominated product with zinc dust and glacial acetic acid.   From these results, it appears that camphoric acid contains two asymmetrical carbon atoms; the theoretical consequences of this view, and its bearing on the question of the constitution of camphor and borneol will be considered subsequently.

Of the remaining seven "camphoric acids" (see above), two, Nos. 5 and 10, have been previously shown by Friedel and Jungfleisch to be mixtures. Chautard's paracamphoric acid (No. 4) is a mixture of i-camphoric acid (3 parts) and i-isocamphoric acid (1 part). Wreden's inactive acid (No. 6) consists of dextrocamphoric acid and lævoisocamphoric acid. Jungfleisch's inactive acid (m. p. 280°, No. 8) is identical with Wreden's meso-acid, and consists of a mixture of dextrocamphoric acid and lævoisocamphoric acid. Armstrong and Tilden's, and Marsh and Stockdale's inactive acids (Nos. 7 and 13) are identical with i-camphoric acid (No. 3). Full details of the preparation, purification, and methods of identification of these compounds are given in the original paper. For purposes of comparison, the three camphoric anhydrides, and bromo- and chlorocamphoric anhydrides, have been prepared, and also the three camphanic acids; the activity of these compounds is of opposite sign to that of the acid from which they are derived. Dextro- and lævo-camphoric anhydrides in chloroform solution at 20° are inactive, in benzene solution optically active; this affords an interesting confirmation of Van't Hoff's statement that in spite of the presence of asymmetrical carbon atoms, a compound may appear inactive, the activity being, however, rendered apparent by change of temperature or of solvent.   J. B. T.

Scammony Resin. By H. SPIRGATIS (*Arch. Pharm.*, **232**, 241—243).—The author cannot admit that the analyses of the barium salt obtained from scammony resin, which were made first by himself and then by Mayer, are incorrect as suggested by Poleck (Abstr., 1893, i, 225).   A. G. B.

Investigation of the Resin of Jalap. By N. KROMER (*Chem. Centr.*, 1894, i, 634—636; from (*Pharm. Zeit. Russ.*, **33**, 1—5, 17—21, 33—37, 49—53, 65—69, 81—85, 97—99).—Mayer ascribed to that part of the resin of the true jalap (*Ipomoea Purga*, Hayne, or *Convolvulus purga*, W.), which is insoluble in ether, the name convolvulin, and the formula (?) $C_{72}H_{60}O_{36}$ + Aq, and to the analogous compound from the spurious jalap the name jalapin. The author has re-examined convolvulin and its derivatives.

Convolvulin forms a colourless, amorphous mass which becomes electrified when rubbed. It is soluble in alcohol and in acetic acid, but insoluble in ether or light petroleum. Its reaction is neutral, and it is coloured red to brownish-red by concentrated sulphuric, nitric, or hydrochloric acid. It melts at 140—148°, and gives a rotation $[\alpha]_D = -36\cdot9°$, and a mol. wt. of 1140—1393. From its analysis and chemical behaviour, the author believes its true formula to be $C_{61}H_{108}O_{27}$.

When treated with bases, barium hydroxide for instance, it yields convolvulinic and methylethylacetic acids. *Convolvulinic acid*, $C_{28}H_{52}O_{14}$, is a white, hygroscopic powder melting at about 180°, and having a rotation $[\alpha]_D = -31\cdot3°$. The *barium salt*, $Ba(C_{28}H_{51}O_{14})_2$ + $2H_2O$, is yellow and amorphous. It is a monobasic acid which forms neutral and basic salts, and also combines with convolvulin.

When hydrolysed with 10 per cent. sulphuric acid, convolvulinic acid is decomposed into a non-crystalline glucose, $C_6H_{12}O_6$, and convolvulinolic acid (m. p. 46°), a monobasic acid isomeric with jalapinolic acid. The convolvulinol obtained by Meyer in this reaction was probably impure convolvulinolic acid. The glucose, on oxidation, yields paragluconic acid. L. T. T.

The Wall-lichen (Parmelia parietina). By R. KOBERT and W. LILIENTHAL (*Chem. Centr.*, 1894, i, 471—472; from *Zeit. Oester. Apoth. Ver.*, **48**, 30—38).—The colouring matter, which the authors consider to be the active principle of this lichen, is very superficially distributed, and may be extracted by means of benzene without destroying the lichen. It crystallises in small, golden-yellow needles which are soluble in alkalis with blood-red coloration. It is more soluble in the ordinary organic solvents than chrysophanic acid, which it was thought to contain by Rochleder and Heldt. The authors consider this colouring matter to be a dihydroxyanthraquinone, and propose for it the name *chrysophyscin*. It is not poisonous, whilst vulpinic acid (with which Bolley considered it to be identical) is poisonous. The colouring matter was termed parietin by Thomsen, and "chrysopykrin" by Stein. The lichen, after extraction of the colouring matter, is not poisonous. L. T. T.

A New Substance Extracted from Lichens. By G. PATERNÒ and F. CROSA (*Gazzetta*, **24**, i, 297—305).—On extracting the lichen, *Lecanora sulphurea* (Schaer), with ether, a mixture containing a resin, usnic acid, rangiformic acid, and a new *substance*, $C_{27}H_{30}O_9,H_2O$, is obtained. The latter is purified by crystallisation from alcohol, benzene, and carbon bisulphide, and is ultimately obtained in white, pearly laminæ melting at 92—93°; the anhydrous substance separates from benzene in minute crystals melting at 123—124°. On cooling the molten mass, it becomes vitreous and melts at about 65°; if this is treated with dilute alcohol, it absorbs water with great development of heat, and yields the hydrate melting at 92—93°. It is readily soluble in cold caustic alkalis, giving solutions which resinify on exposure to air, whilst the alcoholic solution reduces silver nitrate and Fehling's solution, and gives a violet coloration with ferric chloride. The *argento*-derivative, $C_{27}H_{29}O_9Ag$, is obtained as an unstable, gelatinous, white precipitate, which yields the original substance when treated with dilute hydrochloric acid, boiling water, or ethylic iodide. Molecular weight determinations by the cryoscopic method or by Beckmann's method were valueless, the thermometric rise or fall being so small. On boiling the substance with dilute hydrochloric or hydriodic acid, it yields a dehydration *product*, $C_{27}H_{28}O_8,H_2O$, crystallising in colourless, transparent prisms; these effloresce in the air, leaving the anhydrous substance, which melts at 142—143°. This compound is also obtained by warming a solution of the original substance in concentrated sulphuric acid and precipitating with water, or on treating it with acetic chloride or boiling

with sodium carbonate solution. The dehydration product yields normal caproic acid when fused with potash, but gives no argento-derivative. W. J. P.

Scoparin. By G. GOLDSCHMIEDT and F. v. HEMMELMAYR (*Monatsh.,* **15,** 316—361; Abstr., 1893, i, 601).—Acetylscoparin, which has already been described by the authors, sinters at 242° when pure, and melts at 255—256°. It forms hemimorphic crystals belonging to the monoclinic system, $a : b : c = 0.8738 : 1 : 1.3454$; $s = 77° 59'$. The numbers obtained from a long series of analyses and molecular weight determinations show that the compound is *hexacetylscoparin*. *Hexabenzoylscoparin* is a bright, yellow, crystalline compound, and melts at 148—150°.

Ethylscoparin, $C_{19}H_{16}O_8(OMe) \cdot OEt$, reduces Fehling's solution and ammoniacal silver solution when heated with it on the water bath, but is not altered by boiling with alcohol, differing in this respect from scoparin. The *pentacetyl-derivative* crystallises in aggregates of small, white needles, sinters at 120°, and melts at 140—141°.

Methylscoparin has not yet been obtained pure. The product crystallises in beautiful, rhombic plates, sinters at 175°, melts at 185°, and, after solidifying, remelts at 252—253°. The numbers obtained on analysis seem to show that the compound is a mixture of methylscoparin with scoparin, but it does not give the reaction for scoparin with ferric chloride.

Scoparin, when boiled with 6—7 per cent. potassium hydroxide in a reflux apparatus, is partially decomposed with formation of acetovanillone; this crystallises in short, lustrous prisms, melts at 115°, boils at about 300°, and with ferric chloride gives an intense blue coloration. The *acetyl*-derivative forms beautiful, white needles, and melts at 57—58°. The *hydrazone* crystallises in bright, yellow needles, and melts at 125°. When fused with potassium hydroxide, it yields protocatechuic acid. The authors have also examined the behaviour of scoparin when heated with stronger solutions of potassium hydroxide, and have separated from the product, acetovanillone, vanillic acid, protocatechuic acid, and phloroglucinol. The same decomposition products were obtained by allowing scoparin to remain with 10 per cent. potassium hydroxide in a closed vessel for 286 days. When scoparin is boiled with 12 per cent. potassium hydroxide and the mixture is acidified with phosphoric acid and subjected to steam distillation, formic acid is obtained in small quantity.

Ethylscoparin, when treated with potassium hydroxide (10 per cent.), yields a brown oil, from which ethylvanillic acid (m. p. 193°) is obtained on oxidation with potassium permanganate.

When scoparin is boiled with dilute hydrochloric acid, it yields the compound $C_{20}H_{16}O_8 1\frac{1}{2}H_2O$, which has already been obtained by the action of sulphuric acid; it dissolves in dilute potassium hydroxide, and is precipitated unchanged on acidification; but when boiled with 12 per cent. potassium hydroxide, it yields acetovanillone and small quantities of phloroglucinol.

When scoparin is heated above its melting point, it gives off $3\frac{1}{2}H_2O$, whilst ethylscoparin, under similar conditions, gives off $3H_2O$. Both

compounds are reduced by sodium amalgam, yielding dark red, amorphous compounds, which give violet precipitates with lead acetate. The compound obtained from scoparin, on analysis, gave numbers agreeing with the formula $C_{20}H_{26}O_{10}$ or $C_{20}H_{26}O_9$.

The authors were unable to obtain a hydrazine or oxime from scoparin or ethylscoparin. When scoparin is heated with excess of phenylhydrazine at $100°$ and the product is washed with chloroform, a bright yellow, crystalline mass is obtained, which darkens at $225°$, turns black at $235°$, and decomposes violently at $236°$. It gradually decomposes on exposure to the air, giving off phenylhydrazine.

Scoparin forms additive compounds with hydrogen chloride, hydrogen bromide, or bromine, which are very easily decomposed. It has absolutely no physiological action.

The above results show that the constitution of scoparin may be expressed by the formula $OH \cdot C_6H_3(OMe) \cdot C_{13}H_8O_3(OH)_5$ [$= 1 : 3 : 5$], and that in the group $C_{13}H_8O_3(OH)_5$ there is present an atomic complex which is capable of yielding phloroglucinol when treated with potassium hydroxide.   E. C. R.

Red Pigment of Pyrrhocoris Apterus. By C. PHISALIX (*Compt. rend.*, **118**, 1282—1283).—Two litres of the insects, *Pyrrhocoris apterus*, were dried in a vacuum and treated with carbon bisulphide, which dissolves the fatty matter and also the colouring matter. The latter is also dissolved by light petroleum and by alcohol, and the solutions have an absorption spectrum similar to that of carrotene. The solid colouring matter yields a greenish-blue coloration when mixed with concentrated sulphuric acid. It would seem, therefore, that the red pigment of *P. apterus* is very similar to carrotene; it produces no appreciable physiological effect on guinea pigs or mice.
                                                                    C. H. B.

Pyrazole. By L. KNORR (*Annalen*, **279**, 188—232).—The author discusses at length the constitution of benzene and pyrazole; he considers that pyrazole is a tautomeric compound which in its derivatives has the following constitutions.

$$CH{<}^{CH:N}_{CH \cdot NH} \text{ and } CH_2{<}^{CH:N}_{CH:N}.$$
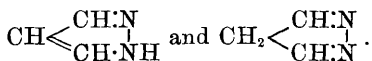
Further, in the case of the first formula, the double bonds may undergo rearrangement, so that the hydrogen atom combined with the one nitrogen atom becomes attached to the other; pyrazole thus behaves as a symmetrical molecule and the 3-methylpyrazole is identical with 5-methylpyrazole, just as 1 : 2 and 1 : 6 di-derivatives of benzene are identical, owing to oscillation of the double bonds in the Kekulé formula.

The author has prepared both 3- and 5-methylpyrazoles by a number of methods which are indicated below, and the identity of the products has been fully established.

3-Methylpyrazole may be prepared by Marchetti's method (Abstr., 1893, i, 179), and by adding hydrazine sulphate and soda to a cooled

solution of sodioformylacetone; dimethylmethylene-hydrazine is also obtained in the latter process.

3 : 5-pyrazoledicarboxylic acid is obtained by the oxidation of 3 : 5-methylpyrazolecarboxylic acid, or of 3 : 5-dimethylpyrazole; it crystallises with $1H_2O$, and is identical with the acid melting at 289°, prepared by Buchner and Papendieck (Abstr., 1893, i, 431; compare Marchetti, *loc. cit.*). The *hydrogen potassium* salt is a characteristic one, it crystallises without water and is sparingly soluble.

Ethylic methylpyrazolecarboxylate is obtained by the condensation of ethylic acetoneoxalate with hydrazine; it crystallises in tables melting at 82—83°, and is readily hydrolysed.

1 : 3-Phenylmethylpyrazole (Claisen and Roosen, this vol., i, 346), yields methylpyrazole on oxidation with alkaline permanganate, and gives 1-*nitrophenyl-3-methylpyrazole* (paranitro?) on treatment with fuming nitric acid; this crystallises in long needles melting at 166°; on reduction with stannous chloride, the nitro-derivative is converted into 1-*amidophenyl-3-methylpyrazole*, $C_{10}H_{11}N_3$, which crystallises in lustrous prisms and melts at 99°. On oxidation with potassium permanganate this substance and also 1-phenyl-5-methylpyrazole, or its amido-derivative, yields methylpyrazole.

1-*Nitrophenyl*-5 : 3-*methylpyrazolecarboxylic acid*, $C_{11}H_9N_3O_4$, obtained by nitrating phenylmethylpyrazolecarboxylic acid, is crystalline and melts at 122—124°. It loses carbonic anhydride at 165—170°, yielding 1-*nitrophenyl-5-methylpyrazole*, which crystallises in lustrous leaflets melting at 161°. The corresponding *amidopyrazole*, obtained by reduction with stannous chloride, crystallises in long prisms melting at 201—202°.

3-*Methylpyrazole platinic chloride*, $(C_4H_6N_2)_2,PtCl_4$, is prepared by crystallising the platinochloride from dilute hydrochloric acid; it forms yellow needles melting and decomposing at 253°. *Argento-methylpyrazole*, $C_4H_5N_2Ag$, is obtained as a voluminous, white precipitate by the action of ammoniacal silver nitrate on the base. 3-*Methyl-pyrazole silver nitrate*, $(C_4H_6N_2)_2,AgNO_3$, crystallises in laminæ melting at 121°. 3-*Methylpyrazole mercuric chloride*, $(C_4H_6N_2)_2,3HgCl_2$, crystallises in needles melting at 165—168°.

Bromo-3-methylpyrazole, obtained by direct bromination of methyl-pyrazole, melts at 67°. Its *hydrobromide*, $C_4H_5N_2Br,HBr$, separates on adding bromine to an aqueous solution of methylpyrazole and crystallises in needles melting at 135°.

4-*Nitro-3-methylpyrazole*, $C_4H_5N_3O_2$, is obtained by heating methyl-pyrazole with a mixture of nitric and sulphuric acids; it crystallises in prisms melting at 134°, and distils at 325° under 748 mm. pressure. The *sodium* and *potassium* derivatives were prepared.

3-*Methylpyrazolesulphonic acid*, $C_4H_5N_2\cdot HSO_3$, is prepared by sulphonating the pyrazole; it is very soluble in water, and melts and decomposes at 257—258°. The *barium* salt is obtained in anhydrous, pearly leaflets.

On heating methylpyrazole with methylic iodide in ethereal solution at 120°, a powerfully odorous *base* of the composition $C_3H_2Me_2N_2$ is obtained; it boils at about 150°, and is possibly a mixture. Excess of methylic iodide reacts with methylpyrazole, yielding a *dimethyl-*

pyrazole methiodide, $C_3H_2Me_2N_2,MeI$; it crystallises in needles and decomposes at 252°. The corresponding *methylic platinochloride*, $(C_3H_2Me_2N_2)_2,Me_2PtCl_6$, decomposes at 225°.

3-Methylpyrazole is oxidised to pyrazole-3-carboxylic acid by potassium permanganate; this acid crystallises in prisms, decomposes into pyrazole and carbonic anhydride at 210—214°, and is doubtless identical with the acid melting at 208—210° obtained by Buchner and Papendieck (*loc. cit.*). W. J. P.

Condensation of Methylhydrazine with β-Diketones. By L. KNORR (*Annalen*, **279**, 232—236).

—1 : 3 : 5-*Trimethylpyrazole*, $C_3N_2HMe_3$, may be prepared by the interaction of methylhydrazine with acetylacetone in aqueous solution or by the action of soda on the methiodide obtained by heating 3 : 5-dimethylpyrazole with methylic iodide. It crystallises in long needles, melts at 37°, and boils at 170° under 755 mm. pressure; its odour recalls that of iodoform, and its aqueous solution has a neutral reaction. The sparingly soluble *picrate* crystallises in prisms melting at 131—133°; the *hydrochloride* is hygroscopic, and crystallises in needles melting at 94—96°. The *aurochloride* with $1H_2O$ is obtained in needles melting at 91—94°, whilst the *platinochloride* melts at 187—191°. No argento-derivative could be prepared, but a double *salt* with mercuric chloride was obtained; it crystallises in six-sided leaflets melting at 164—169°. 1 : 3 : 5-*Trimethyl-4-nitropyrazole*, prepared by direct nitration of the pyrazole, crystallises in needles melting at 56—57°.

1 : 3 : 4 : 5-*Tetramethylpyrazole* is obtained by the condensation of methylhydrazine with methylacetylacetone; it boils at 190—193°, solidifies in the ice-chest, and has a more unpleasant odour than 1 : 3 : 5-trimethylpyrazole.

1 : 5-*Dimethylpyrazolone* may be prepared by the condensation of methylhydrazine with ethylic acetoacetate; it melts at 106—109°, and boils at 205—210° under 210 mm. pressure. W. J. P.

Condensation of Hydrazine with Methylacetylacetone. By B. OETTINGER (*Annalen*, **279**, 244—246).

—3 : 4 : 5-*Trimethylpyrazole*, $C_3HMe_3N_2$, is formed by the action of hydrazine hydrate on methyl-acetylacetone; it boils at 232—233° under 753 mm. pressure, and crystallises in six-sided leaflets melting at 137—138°. It is volatile in a current of steam and sublimes at 100°. The *hydrochloride* crystallises in minute needles, decomposes at about 265°, and, with mercuric chloride, gives a double salt, $C_6H_{10}N_2,2HgCl_2$, melting at 193—196°. The *picrate* crystallises in needles melting at 237—239°, whilst the double *salt* with silver nitrate, $(C_6H_{10}N_2)_2,AgNO_3$, crystallises in needles melting at 221°; the *argento*-derivative, $C_6H_9N_2Ag$, was also prepared.

On heating the base with methylic iodide, 1 : 3 : 4 : 5-tetramethylpyrazole is obtained; its *methiodide*, $C_7H_{12}N_2,MeI$, crystallises in needles melting at 192° whilst its *methylic platinochloride*,

$$(C_7H_{12}N_2)_2,Me_2PtCl_6,$$
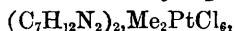
melts and decomposes at 215—216°. W. J. P.

Condensation of Hydrazine with Dimethylacetylacetone.
By L. KNORR and B. OETTINGER (*Annalen*, **279**, 247—248).—
3 : 4 : 4 : 5-*Tetramethylpyrazole*, $\begin{matrix} N:CMe \\ | \\ N:CMe \end{matrix}{>}CMe_2$, is obtained by the
action of hydrazine hydrate on dimethylacetylacetone; it boils at
242—243° under 740 mm. pressure, and melts at 50—55°. This sub-
stance is typical of the symmetrical tautomeric constitution assigned
to pyrazole by Knorr (this vol., i, 544).   W. J. P.

**Condensation of Hydrazine with Benzoylacetone and Ethylic
Benzoylacetoacetate.** By B. SJOLLEMA (*Annalen*, **279**, 248—256).
—3 : 5-*Methylphenylpyrazole*, $CH{<}\begin{matrix} CPh:N \\ | \\ CMe \cdot NH \end{matrix}$, may be prepared by the
action of hydrazine hydrate on benzoylacetone; it crystallises in
needles melting at 128°, and boils at 326—327° (cor.). The *hydro-
chloride* is obtained as a crystalline powder, melting at 205°; the
platinochloride and the *picrate* crystallise in yellow needles. The
acetyl-derivative forms needles melting at 43°, and is hydrolysed by
heating with soda. The *dibromide*, $C_{10}H_{10}N_2Br_2$, is obtained by direct
bromination, and crystallises in needles melting at 205°; when
heated with water, it yields 3 : 5-phenylmethyl-4-bromopyrazole
melting at 93°.

On heating the base with methylic iodide, a *phenyldimethylpyrazole
methiodide*, $C_{11}H_{12}N_2$,MeI, which melts at 190°, is obtained; the
methochloride and the *methylic platinochloride*, $(C_{11}H_2N_2)_2$,Me$_2$PtCl$_6$,
crystallise in needles melting at 50° and 216° respectively. On
oxidising 3 : 5-phenylmethylpyrazole with potassium permanganate,
a *phenylpyrazolecarboxylic acid*, which melts and decomposes at
230—240°, is obtained.

Ethylic 3 : 5-*phenylmethylpyrazole-4-carboxylate* and 3-phenylpyr-
azolone result from the condensation of hydrazine hydrate with
ethylic benzoylacetoacetate. The free *acid*, which crystallises in
needles, decomposes at 260—265°, and on distillation yields car-
bonic anhydride and 3 : 5-phenylmethylpyrazole. The *silver* and
barium salts are both amorphous. The acid yields 5-phenylpyrazole-
3 : 4-dicarboxylic acid on oxidation with permanganate; this melts
and decomposes at 235°, and seems to be identical with the dicarb-
oxylic acid prepared by Buchner and Fritsch (Abstr., 1893, i, 281),
since both acids give the same phenylpyrazole melting at 78° on dis-
tillation. The latter can only be 5-phenylpyrazole, and not 4-phenyl-
pyrazole, as stated by these authors. Further, the substance melting
at 228°, described by Buchner and Dessauer (Abstr., 1893, i, 282) as
5-pyrazole, must be the 4-isomeride. 5-*Phenylpyrazole picrate* crystal-
lises in needles, melting at 168°.   W. J. P.

**Condensation of Hydrazine with Acetylacetone, Ethylic
Acetylacetoacetate, and Ethylic Ethylideneacetoacetate.** By
G. D. ROSENGARTEN (*Annalen*, **279**, 237—243).—3 : 5-Dimethyl-
pyrazole is obtained in quantitative yield by the action of hydrazine
hydrate on acetylacetone (Marchetti, Abstr., 1893, i, 177); the

argento-derivative crystallises in long needles melting at 152°. On heating the pyrazole with methylic alcohol and methylic iodide at 100—110°, 1 : 3 : 5-*trimethylpyrazole methiodide* is obtained (compare preceding abstracts); it crystallises with 1CHCl₃. The *methylic platinochloride*, (C₆H₁₀N₂)₂,Me₂PtCl₆, crystallises in long needles, melting at 222°.

Ethylic ethylideneacetoacetate or ethylic acetylacetoacetate interacts with hydrazine hydrate, forming *ethylic* 3 : 5-*dimethylpyrazole-4-carboxylate*, 3-methylpyrazolone, and the substance of the composition $C_8H_8N_2O_2$, previously described by Knorr (Abstr., 1887, 601); the compound last named is also obtained by the action of hydrazine hydrate on ethylic acetoacetate. In the action between ethylic ethylideneacetoacetate and hydrazine hydrate, 4-*ethylidene-bis-3-methylpyrazolone* (?),

$$NH<^{N\,=\,CMe}_{CO-CH\cdot CHMe\cdot CH\cdot CO}>^{CMe:N}NH,$$ is also obtained; it crystallises in prisms, and melts and decomposes at 255°.

Ethylic 3 : 5-dimethylpyrazole-4-carboxylate crystallises with 2H₂O, and then melts at 60°, but when anhydrous it melts at 96°. It sublimes on the water-bath, and is volatile in a current of steam. The corresponding *acid* crystallises in small needles or leaflets, and melts and decomposes at 290°. On distillation or heating with water at 200°, it yields dimethylpyrazole and carbonic anhydride, whilst on oxidation with alkaline permanganate, it gives 3 : 4 : 5-pyrazole-tricarboxylic acid. W. J. P.

Action of Chloride of Sulphur on Acetylacetone. By A. ANGELI and MAGNANI (*Gazzetta*, **24**, i, 342—370).

—Sulphur dichloride and acetylacetone interact violently with formation of *thioacetyl-acetone*, CHAc₂·S·CHAc₂; this crystallises in very beautiful, colourless, orthorhombic prisms melting at 67—72°; $a : b : c = 0.9412 : 1.7239$. Thioacetylacetone behaves like an acid, reddening litmus, decolorising phenolphthaleïn, and dissolving in soda, ammonia, or alkaline carbonates; it is precipitated from these solutions by hydrochloric acid, although slight decomposition occurs even in the cold, and becomes complete on boiling. Aqueous alcoholic solutions of the substance give precipitates with salts of copper or lead, but not with those of barium; with ferric chloride, a beautiful red colour is produced.

Thiodimethylisoxazole (?), $^{N:CMe}_{O\cdot CMe}>C\cdot S\cdot C<^{CMe:N}_{CMe\cdot O}$, is obtained on boiling an alcoholic solution of thioacetylacetone with hydroxylamine hydrochloride; sulphurous anhydride is evolved, and the oxazole is ultimately obtained in colourless, lamellar crystals melting at 127—128°.

Thiodimethylphenylpyrazole, $^{NPh\cdot CMe}_{N=CMe}>C\cdot S\cdot C<^{CMe\cdot NPh}_{CMe:N}$, is prepared by boiling thioacetylacetone with phenylhydrazine in acetic acid solution; it forms small, lustrous, colourless crystals melting at 114°.

2 *q* 2

Dithioacetylacetone (this vol., i. 209) also crystallises in the ortho-rhombic system; $a : b : c = 0.9317 : 1 : 1.6501$. Its aqueous alco-holic solution possesses a distinctly acid reaction, and gives preci-pitates with salts of copper or lead, but not with those of barium; it gives a red coloration with ferric chloride.

Trithioacetylacetone, $CHAc_2\cdot S_3\cdot CHAc_2$, is prepared by the action of sulphur monochloride on acetylacetone; the action is violent, and the product, after purification, is obtained in almost colourless, ortho-rhombic plates, melting at $130°$; $a : b : c = 0.7062 : 1 : 1.6797$. A very distinct morphotropic relationship exists between the crystals of these three thio-compounds. Trithioacetylacetone behaves as an acid, just as the mono- and di-thio-derivatives. On treatment with hydr-oxylamine hydrochloride, it yields *trithiodimethylisoxazole*,

$$\begin{matrix} N\vdots CMe \\ | \\ O\cdot CMe \end{matrix}\Big>C\cdot S\cdot S\cdot S\cdot C\Big<\begin{matrix} CMe\vdots N \\ | \\ CMe\cdot O \end{matrix};$$
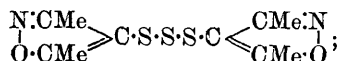
this crystallises in beautiful, colourless needles, and melts at $65-66°$. Trithioacetylacetone is converted into *trithiodimethylphenylpyrazole*,

$$\begin{matrix} N\!=\!\!=\!CMe \\ | \\ NPh\cdot CMe \end{matrix}\Big>C\cdot S_3\cdot C\Big<\begin{matrix} CMe\vdots N \\ | \\ CMe\cdot NPh \end{matrix},$$ by the action of phenylhydrazine; it

is a crystalline powder, and melts at $141°$. W. J. P.

Pyrazine. By L. WOLFF (*Ber.*, **27**, 2018—2019).—Attention is drawn to the discrepancy existing between the author's description of pyrazine (Abstr., 1893, i, 373) and that of Stoehr (*loc. cit.*, 486). In support of his views, the author points out that not only do Stoehr's later results differ widely from those already given by that investi-gator, but that the specimen of pyrazine obtained by Gabriel and Pinkus from amido-aldehyde (*loc. cit.*, 734) agrees closely in melting point and boiling point with the base described by the author.

M. O. F.

Combination of Pyridine with Permanganates. By T. KLOBB (*Compt. rend.*, **118**, 1271—1273).—Pyridine, like ammonia, forms crystalline compounds with silver, copper, cadmium, zinc, and nickel permanganates. They are more or less soluble in water, and very soluble in pyridine; when heated rapidly they explode, but when heated slowly, no explosion takes place. When moistened with sulph-uric acid, or when suddenly compressed, they burn vigorously. Even at low temperatures they lose pyridine, and undergo partial oxidation; they should be prepared and dried at about $0°$.

The silver compound, $AgMnO_4,2C_5NH_5$, is obtained on adding a small quantity of pyridine to an aqueous solution of silver nitrate and potassium permanganate mixed in equivalent proportions. It is only very slightly soluble in water, and forms violet, microscopic crystals, which decompose at $65°$. The other compound,

$$2AgMnO_4,5C_5NH_5,$$
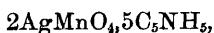
is obtained by pouring the mixed saline solutions into an excess of pyridine, or by gradually adding water to a 50 per cent. solution of silver permanganate in pyridine. It forms violet needles, which only explode at about $100°$.

The copper salt, $Cu(MnO_4)_2,4C_5NH_5$, is obtained in the same manner as the first silver salt, and forms beautiful, violet crystals, which decompose at 65°. The cadmium salt, $Cd(MnO_4)_2,4C_5NH_5$, must be prepared from concentrated solutions at 0°, and forms tabular crystals, apparently rhombic; it decomposes at 65°. Both the zinc and nickel compounds are similar in composition, and are prepared in a similar manner. The nickel salt occurs as a violet, crystalline powder, or in nodules, and decomposes at 65°. Cobalt permanganate does not yield a similar compound. C. H. B.

Additive Product of Pyridine and Chloracetone. By H. DRESER (*Arch. Pharm.*, **232**, 183—186).—These two substances react to form a crystalline *compound*, $C_5NH_5Cl \cdot CH_2 \cdot COMe$. The *mercurochloride* of this substance crystallises in white needles, and melts at 119° (uncor.); the *picrate* melts at 141° (uncor.); the *platinochloride* melts and decomposes at 206—207° (uncor.); and the *aurochloride* at 136—138° (uncor.).

Quinoline did not yield an analogous product. A. G. B.

Synthesis of Pyridine Derivatives from Aldehydes and Benzoylpiperidine. By L. RÜGHEIMER (*Annalen*, **280**, 36—49).— The condensation of benzoylpiperidine with two molecular proportions of an aldehyde is accompanied by the elimination of the benzoyl group and 2 atoms of hydrogen; thus

$$C_5NH_{10} \cdot COC_6H_5 + 2C_6H_5 \cdot COH = C_{19}H_{17}N + C_6H_5 \cdot COOH + H_2 + H_2O.$$
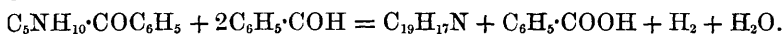
Simultaneously 2 atoms of hydrogen migrate from the piperidine nucleus to the aldehydic groups, 3 : 5-disubstituted derivatives of pyridine being formed, whilst the liberated hydrogen reduces a portion of the aldehyde employed, with formation of the parent hydrocarbon.

3 : 5-*Dibenzylpyridine*, $C_5NH_3(CH_2Ph)_2$, is obtained by heating 6 parts of benzaldehyde with 5 of benzoylpiperidine in a closed tube for six hours at 240—250°. The base is slightly soluble in water and readily in alcohol, crystallising from the latter in thin plates, which melt at 89°, the liquid boiling at 300°; its basic character is but feeble, and the salts are decomposed by water. Dibenzylpyridine remains unchanged when heated at 125° with strong caustic soda, whilst dilute hydrochloric acid at 210° merely transforms it into the *hydrochloride*, melting at 164·5—166°, and characterised by its low solubility in boiling benzene and the feathery aggregates in which it crystallises. On adding water to the alcoholic solution of this salt, the base is deposited as an oil, which soon solidifies. Strong hydrobromic acid at 175—180° slightly alters the base, but at lower temperatures the *hydrobromide* alone is formed; this crystallises from hot benzene in thin tablets which melt at 148·5°. The *nitrate* melts at 96·5—98°. The *methiodide* was obtained in the form of an oil which yields an unstable molecular compound with chloroform, crystallising in plates. The *ethiodide* is deposited from alcohol in nodular aggregates of needles, and melts at 137°.

Tribenzylpyridine, $C_5NH_2(CH_2Ph)_3$, which occurs as a bye-product

in the preparation of the dibenzyl-derivative, remains undissolved when the crude substance is treated with ether. It is with difficulty soluble in hot amylic alcohol, separating from this solvent in hexagonal plates which melt at 278—280°.

3 : 5-*Dibenzoylpyridine*, $C_5NH_3Bz_2$, is formed by the oxidation of 3 : 5-dibenzylpyridine; chromic acid is the agent employed, the base being scarcely attacked by potassium permanganate, even when heated with a strong solution of it. Dibenzoylpyridine forms long needles melting at 123°; it yields an *oxime*, and the *platinochloride* forms blunt, bright red needles. It possesses slightly basic properties, dissolving in dilute mineral acids when heated.　　　　　M. O. F.

3-Benzoylpyridine-5-carboxylic acid, $COPh \cdot C_5NH_3 \cdot COOH$, and the Position of the Benzyl Group in Dibenzylpyridine. By L. Rügheimer and W. Kronthal (*Annalen*, **208**, 50—59).—This acid is the intermediate product in the oxidation of dibenzoylpyridine to dinicotinic acid. It separates from hot benzene in colourless needles, and melts at 199—201°; the *silver* and *copper* salts are well defined.

Paradinitro-3 : 5-*dibenzylpyridine*, prepared by adding the base in small quantities at a time to fuming nitric acid, forms yellowish needles which melt at 144—146°; its constitution is shown by the fact that the only nitrobenzoic acid formed on oxidation is the para-modification. It is sufficiently basic in character to form salts; the *nitrate* crystallises in colourless needles, and melts at 160—162°; the *hydrochloride* melts at 121—123°; the *platinochloride* melts at 225—226°. The *picrate*, which is almost insoluble in alcohol, melts at 175—177°; the *methiodide* at 190—193° and the *ethiodide* at 167—173°.

Paradiamido-3 : 5-*dibenzylpyridine* is obtained by reducing the dinitro-compound with stannous chloride and hydrochloric acid. It is insoluble in light petroleum, but dissolves in amylic alcohol, benzene, and alcohol, separating from the latter in needles which melt at 155—157°; the *hydrochloride* remains unfused at 250°. On oxidising diamidodibenzlpyridine with potassium permanganate, dinicotinic acid is formed; this result shows conclusively that the substituted pyridines obtained by the action of aldehydes on benzoylpiperidine are 3 : 5-derivatives.　　　　　M. O. F.

Cuminaldehyde and Benzoylpiperidine (by L. Rügheimer and W. Herzfeld, *Annalen*, **280**, 60—73) **and the Isomeric Toluyl-aldehydes and Benzoylpiperidine** (by L. Rügheimer and K. Döring, *Annalen*, **280**, 76—78).—When cuminaldehyde and benzoyl-piperidine are heated in a closed tube for eight hours at 235—240°, derivatives analogous to those described in the foregoing abstracts are obtained, accompanied by small quantities of cymene.

Paradiisopropyl-3 : 5-*dibenzylpyridine*, $C_5NH_3(CH_2 \cdot C_6H_4Pr^\beta)_2$, melts at 76—77°; it is feebly basic, the salts being decomposed by water. The *hydrochloride* melts at 182—183°. The *picrate*,

$$C_{25}H_{29}N, C_6H_2(NO_2)_3 \cdot OH,$$
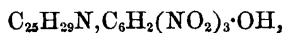
is soluble in alcohol, and melts at 111—113°. The *platinochloride* decomposes at 230—236° ; the *aurochloride* forms deliquescent, yellow needles. The base yields crystalline *double salts* with mercuric chloride, cadmium chloride, and copper acetate, the latter forming bluish-violet crystals of the constitution $C_{25}H_{29}N,C_2H_4O_2,Cu(C_2H_8O_2)_2$. The *methiodide* is soluble in water, and melts at 173—174° ; the *ethiodide* at 168—169°. The *methochloride* was obtained in crystalline scales which could not be recrystallised ; the *platinochloride* of this salt melts at 216—219°. The oxidation of diisopropyldibenzylpyridine is carried out by means of chromic acid, 3 : 5-*dibenzoylpyridine-paradicarboxylic acid* being formed. This bibasic acid is insoluble in water, alcohol, and ether, but may be recrystallised from hot glacial acetic acid ; it melts at 308°, decomposition and partial sublimation taking place simultaneously. The *ammonium* salt undergoes decomposition when its solution is evaporated, but the *calcium, copper,* and *silver* salts are well-defined. When the last-named is distilled alone in small quantities, 3 : 5-dibenzoylpyridine is formed (compare Koenigs, Abstr., 1892, 293).

Paratriisopropyltribenzylpyridine, $C_5NH_2(CH_2 \cdot C_6H_4Pr^\beta)_3$, is separated from the mixture of bases by means of its insolubility in ether ; it melts at 299—302°. In addition to this compound, *paraisopropylbenzylpyridine* occurs as a bye-product in the preparation of the disubstituted compound ; it was obtained as an oil, and its *platinochloride* forms rectangular plates which melt at 208—213°.

The derivatives obtained from the three isomeric tolyl aldehydes, in every way analogous to those already described, may be tabulated as follows.

	Diparaxylylpyridine.	Dimetaxylylpyridine.	Diortho-xylylpyridine.
Base, $C_{21}H_{21}N$	m. p. 108·5°	m. p. 65—66·5°	m. p. 40·5°
Hydrochloride, $C_{21}H_{21}N,HCl$	180—182°	165—166°	191—104°
Platinochloride, $(C_{21}H_{21}N)_2,H_2PtCl_6$	252—255	185—186	171—174
Picrate, $C_{21}H_{21}N,C_6H_2(NO_2)_3 \cdot OH$	156—158	116—117	182—183
Methiodide, $C_{21}H_{21}N,MeI$	137°	105—107	152—153
Ethiodide, $C_{21}H_{21}N,EtI$	148—150	109—109·5°	148—142

The acid obtained by the oxidation of diparaxylylpyridine is identical with that derived from paradiisopropyl-3 : 5-dibenzylpyridine. From dimetaxylylpyridine, however, is obtained 3 : 5-*dibenzoylpyridine-metadicarboxylic acid ;* this forms minute needles, which melt at 270—271°.   M. O. F.

Anderson's Pyridine Reaction. By A. Cossa (*Gazzetta*, **24**, i, 393–397 ; compare Abstr., 1893, i, 364).—The term "Anderson's

reaction " is usually applied to the elimination of hydrogen chloride and formation of a platinopyridine chloride, $(C_nH_{2n-5}N)_2PtCl_4$ (Anderson's platinic compound), which occurs on boiling an aqueous solution of a pyridine platinochloride $(C_nH_{2n-5}N)_2,H_2PtCl_6$. The author finds that a similar reaction occurs with the platinosochlorides.

Pyridine platinosochloride, $(C_5H_5N)_2,H_2PtCl_4$, is deposited on strongly cooling a mixed solution of potassium platinosochloride and pyridine hydrochloride; it crystallises in anhydrous monosymmetric prisms, and is very soluble in water, but insoluble in alcohol. On boiling its aqueous solution, or on heating the solid substance at 130°, platososemidipyridine chloride, $(C_5H_5N)_2PtCl_2$ (Anderson's platinous compound), is deposited. If the boiling is not too prolonged, a double *salt* of the composition $(C_5H_5N)_2PtCl_2,(C_5H_5N)_2,H_2PtCl_4$ is formed; it crystallises in long, yellow prisms. Both the platinosochloride and the platinochloride also decompose slowly in aqueous solutions at the ordinary temperatures, giving Anderson's platinous and platinic compounds respectively.

The platinous compound is converted into the platinic compound by digesting it with nitro-hydrochloric acid at 100°. Anderson's statement that platosopyridine chloride is obtained by treating platinosemidipyridine chloride with pyridine is inexact; a diplatinous compound seems to be formed.   W. J. P.

Synthesis of Quinoline.

By V. KULISCH (*Monatsh.*, **15**, 276—279).—Quinoline is obtained by adding an aqueous solution of sodium hydroxide (1 : 2) to a solution of glyoxal in an excess of orthotoluidine, and heating the mixture in a reflux apparatus at 150° for $1\frac{1}{2}$ hours. The yield amounts to 35—40 per cent. of that required by theory. Other dehydrating agents, such as concentrated sulphuric acid and zinc chloride, give extremely bad yields.

The author is engaged in an examination of products of condensation of α-diketones and α-ketonic acids with orthotoluidine with the object of obtaining derivatives of quinoline.   E. C. R.

Synthesis of Isoquinoline.

By E. BAMBERGER and C. GOLDSCHMIDT (*Ber.*, **27**, 1954—1957).—Isoquinoline is obtained when syn-cinnamaldoxime is heated with phosphoric anhydride at 60—70°. Anti-cinnamaldoxime, which is also obtained in the preparation of cinnamaldoxime, likewise yields isoquinoline under the same conditions.

A very small quantity of quinoline is obtained on heating cinnamaldehyde hydrazone with acetic anhydride at 215—225, and also by passing dry hydrogen chloride through the melted hydrazone; in the latter process, a small quantity of a bye-product is also obtained, which melts at 135°, and is apparently a hydrazone.   E. C. R.

Synthesis of Isoquinoline and its Derivatives.

By C. POMERANZ (*Monatsh.*, **15**, 299—306; Abstr., 1893, i, 607).—The author has continued his researches on the production of isoquinoline from benzaldehyde and amidoacetal, and has obtained a yield equal to 50 per cent. of that required by theory. Benzylideneamidoacetal

is mixed with well-cooled, concentrated sulphuric acid (3 parts), and the mixture gradually added to 3 parts of sulphuric acid heated at 160°. Other condensation agents which the author employed gave very bad results.

α-Methylisoquinoline is obtained in a similar way from acetophenone and amidoacetal; but the yield only amounts to 15 per cent. of that required by theory. The product, which is isomeric with γ-methyl-isoquinoline obtained from methylbromophthalimide, is a colourless liquid, boils at 248° (uncor.), and has an odour between that of pyridine and quinoline. The *platinochloride* crystallises in bright red prisms with $4H_2O$, and, when anhydrous, melts and froths up at 210°. The *sulphate* crystallises in flat, colourless prisms, and melts at 246—247°. The *dichromate* crystallises in yellowish-red prisms, and decomposes at 145. E. C. R.

2 : 4-Dibromoquinoline. By A. CLAUS and A. AMMELBURG (*J. pr. Chem.*, [2], **50**, 29—37).—2 : 4-Dibromoquinoline melts at 112°, not 110° (Abstr., 1890, 172). The *methiodide* melts at 287°; the *methochloride* becomes discoloured at 145° and melts at 236°, whilst its *platinochloride* decomposes and melts at 249°. The *hydrobromide* of 2 : 4-dibromoquinoline melts at 288°; its *perbromide*, $C_9NH_5Br_2,HBr,Br_2$, obtained by brominating the hydrobromide in ether, forms orange tables, melting at 215°. By heating the perbromide with bromine at 200°, 2 : 4 : 4′-*tribromoquinoline* is obtained as the chief product; this crystallises in colourless needles and melts at 125—126°; a more highly brominated compound (colourless needles, m. p. 148°) is formed at the same time. The *platinochloride* of 2 : 4 : 4′-tribromoquinoline was prepared, but the base is too feeble to form a methiodide.

1 : 2 : 4-*Nitrodibromoquinoline* is the sole product of the nitration of 2 : 4-dibromoquinoline; it crystallises in short, colourless prisms and plates, and melts at 198°; the *platinochloride* becomes dark at 220°, melting at 291°. By reduction, the nitro-derivative easily passes into 1 : 2 : 4-*amidodibromoquinoline*, which crystallises in colourless needles and melts at 127°; the *hydrochloride* melts at 191°; the *platinochloride* is also described.

1 : 2 : 4-*Tribromoquinoline*, obtained from the above amido-derivative through the diazo-reaction, crystallises in colourless, lustrous needles, melts at 141°, and sublimes; no methiodide could be obtained, but the *platinochloride* was prepared, and was found to melt and decompose at 280°. A discussion as to the orientation of this tribromoquinoline concludes the paper. A. G. B.

Condensation Products of Ortho- and Para-hydroxybenzaldehyde with Quinaldine. By S. DZIERZGOWSKI (*Ber.*, **27**, 1979—1983).—Salicylethylenequinoline has been previously obtained by Wallach and Wüsten (*Ber.*, **16**, 2007) from quinaldine and ortho-hydroxybenzaldehyde; it is insoluble in alkali carbonates, dissolves in acids with an orange colour, does not reduce copper or silver solutions, and gives no coloration in alcoholic solution with ferric chloride. The *hydrochloride* crystallises in orange-red needles with 1 or $1\frac{1}{2}H_2O$

according to circumstances, melts and decomposes at 255—260°, and undergoes dissociation on prolonged boiling with water. The salt gives a series of yellow, amorphous precipitates with the ordinary alkaloïd reagents. The *sulphate*, *acetate*, *oxalate*, and *tartarate* are crystalline and sparingly soluble. *Salicylethyltetrahydroquinoline*, $C_{17}H_{19}NO$, is prepared by the reduction of the quinoline by means of sodium, and crystallises in colourless, slender needles, melting at 121°. The base reduces silver, but not copper, solutions, dissolves in concentrated sulphuric acid without coloration, and is oxidised to a red dye by nitric acid. The *hydrochloride* crystallises in prismatic plates, melts at 223—225°, gives, with ferric chloride, a yellowish coloration, changing to brown ; phosphomolybdic acid and phosphotungstic acid produce white, amorphous precipitates, potassium bismuthoiodide, mercuroiodide, and cadmioiodide give yellow precipitates.

Parahydroxybenzethylenequinoline gives no coloration with ferric chloride. Cryoscopic molecular weight determinations in phenol agree with the formula $C_{17}H_{13}NO$. The *hydrochloride* crystallises with $1\frac{1}{2}H_2O$ in purple-reddish needles, and melts and decomposes at 264—266°. *Parahydroxyethyltetrahydroquinoline* is prepared in a similar manner to the ortho-derivative ; it crystallises in colourless rhombohedra melting at 115°, and reduces silver solutions on boiling. The *hydrochloride* crystallises in colourless needles, and melts at 282° ; with ferric chloride, it gives an olive-brown coloration, changing to purple-red, and white precipitates with phosphotungstic and phosphomolybdic acids. Ortho- and para-benzethylenequinoline readily combine with bromine to form compounds, which are being further investigated.

<div align="right">J. B. T.</div>

Anthrapyridinequinones. By A. PHILIPS (*Ber.*, **27**, 1923—1927).—Bernthsen and Mettegang have shown (Abstr., 1887, 737) that quinolinic anhydride is converted into 3-benzoylpicolinic acid by the action of benzene and aluminium chloride, but they were unable to bring about the condensation of the acid into an anthrapyridine-quinone analogous to the conversion of orthobenzoylbenzoic acid into anthraquinone. The author has carried out a similar series of reactions with an isomeride of quinolinic acid, namely, cinchomeronic acid, and has succeeded in obtaining β-anthrapyridinequinone in quantity.

When cinchomeronic anhydride is heated with benzene and aluminium chloride, it is converted into 4-*benzoylnicotinic acid*,

$$C_5NH_3Bz \cdot COOH,$$
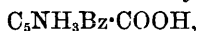
which forms a yellowish, crystalline mass, melts at 216°, and sublimes partly undecomposed ; at 260°, however, it evolves carbonic anhydride, and is converted into a *phenyl pyridyl ketone*, $C_5NH_4 \cdot COPh$; this is isomeric with the ketone obtained from 3-benzoylpicolinic acid by Bernthsen and Mettegang, so that the new ketone, and the acid from which it is obtained, must contain the benzoyl group in the 4-position. To convert the acid into *anthrapyridylquinone*, it is heated with concentrated sulphuric acid at 175°, and the brown solution after being poured into water, is neutralised with ammonia. The precipitated quinone, when recrystallised from carbon tetrachloride, forms needles,

melting at 170°, and subliming, on careful heating, in long needles, resembling those of anthraquinone. It dissolves in dilute acids, and, on treatment with zinc dust and aqueous soda, gives a wine-red solution. Two isomeric anthrapyridinequinones are possible, namely,
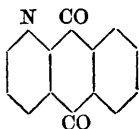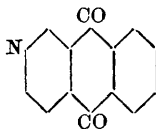
α-Anthrapyridylquinone.   β-Anthrapyridylquinone.

As the above ketone is formed from a 4-benzoyl-compound, it must be the β-derivative.

The β-derivatives being so readily obtained, the author has repeated Bernthsen and Mettegang's experiments with 3-benzoylpicolinic acid. The results obtained show that, contrary to the statement of these investigators, *α-anthrapyridylquinone* is, in reality, obtained on heating the 3-benzoyl compound with sulphuric acid at 270°; the yield is, however, extremely small. It crystallises in needles, melts at 280°, and sublimes in flat needles of a pure yellow colour. With zinc dust and aqueous soda, it forms a dark blue solution.   H. G. C.

Constitution of Dimethylpiperidine and its Homologues.

By A. LADENBURG, M. MUGDAN, and O. BRZOSIOVICZ (*Annalen*, **279**, 344—366).—Dimethylpiperidine (Hofmann, Abstr., 1888, 813), when treated with hydrogen chloride at 220°, is converted into dimethyl-pyrrolidine, $CH_2 <^{CH_2-CH_2}_{NMe\cdot CHMe}$. If the trimethylpyrrolidinium hydroxide, prepared from this base by the action of methylic iodide and silver oxide, is distilled, it decomposes into water and the original dimethylpiperidine. Dimethylpyrrolidine hydrochloride, moreover, loses methylic chloride when heated in a stream of hydrogen chloride, methylpyrrolidine being formed. The platinochloride of this compound melts at 172—173°, the *aurochloride* at 212°. This behaviour is in agreement with the results previously obtained by Merling (Abstr., 1891, 1506), and confirms the formula $CH_2{:}CH\cdot[CH_2]_3\cdot NMe_2$, which has been given to dimethylpiperidine.

Dimethylconiine, when treated in a similar manner, behaves differently, and is converted into coniine. Dimethylconiine itself is strongly dextrorotatory, $[α]_D = +17\cdot04$, and, therefore, should contain an asymmetric carbon atom. The formula $CHPr{:}CH\cdot[CH_2]_3\cdot NMe_2$, which expresses its relation to dimethylpiperidine, does not fulfil this condition, whilst the alternative formula $CH_2{:}CH\cdot CH_2\cdot CH_2\cdot CHPr\cdot NMe_2$ fails to express the different behaviour towards hydrogen chloride. The only formula which satisfies both of these conditions is the following, $NMe_2\cdot CH <^{CH_2-CH_2}_{CHPr\cdot CH_2}$. Dimethyl-α-pipecoline, like coniine, is not converted by hydrogen chloride into a pyrrolidine derivative, but yields methyl-α-pipecoline. From analogy with dimethylconiine, therefore, the formula of dimethylpipecoline should be

$$NMe_2 \cdot CH < \begin{matrix} CH_2 - CH_2 \\ CHMe \cdot CH_2 \end{matrix}.$$
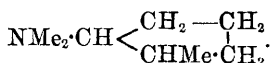
The authors have now found that dimethylpipecoline is optically active, although only to a very slight degree, and this is in accordance with this formula, which contains an asymmetric carbon atom. The analogy between dimethylpiperidine and dimethylconiine is, however, not brought out by the new formula for the latter, although the two bases are in many respects very similar. Thus dimethylconiine, like dimethylpiperidine, unites with 2 atoms of iodine to produce a *diiodide*, $C_{10}H_{21}NI_2$, which forms white crystals melting at 184°, and, on treatment with silver chloride, forms a *chloriodide*, $C_{10}H_{21}NICl$, the *platinochloride* of which can be obtained in the crystalline form. The new formula, moreover, does not explain the ease with which the hydrochlorides of dimethylconiine and dimethylpipecoline unite with 1 mol. of hydrogen chloride.   A. H.

Piperidylacetal. By 'R. STOERMER and O. BURKERT (*Ber.*, **27**, 2016—2018).—*Piperidylacetal*, $C_5NH_{10} \cdot CH_2 \cdot CH(OEt)_2$, is formed when monochloracetal is heated with piperidine (2 mols.) until piperidine hydrochloride no longer separates. The pure base boils at 219—221° (uncorr.); the *hydrochloride* is deliquescent, the *platinochloride* crystallises in orange needles, which melt at 134°, and the *aurochloride* melts at 96°. The *methiodide* and *ethiodide* melt at 119° and 123° respectively, and additive compounds have been also obtained with propylic bromide, allylic iodide, and monochloracetone. A cold silver solution is quickly attacked by the base, which also slightly reduces Fehling's solution when heated.   M. O. F.

Sulphonepiperidide and its Oxidation Product Sulphone-δ-Amidovaleric acid. By A. TÖHL and F. FRAMM (*Ber.*, **27**, 2012—2016).—Sulphuryl chloride reacts with piperidine as with secondary amines, forming *sulphonepiperidide*, $SO_2(NC_5H_{10})_2$, which crystallises from dilute alcohol in large, lustrous plates, melts at 93°, and boils at 230°. It is not affected by boiling with soda or concentrated hydrochloric acid, but at 200° is resolved by the latter into sulphuric acid and piperidine. The yield is about 50 per cent. of the theoretical. The *tetrabromo-derivative* is deposited from glacial acetic acid in lustrous crystals, melting and decomposing at 203—204°. By the action of chlorine in excess on sulphopiperidide in glacial acetic acid, *tetrachlorosulphonepiperidone*, $SO_2[N < \begin{matrix} CH_2 \cdot CH_2 \\ CO \cdot CHCl \end{matrix} > CHCl]_2$, is formed; it crystallises from dilute alcohol in colourless plates, melts at 158° and is being further investigated. *Sulphone-δ-amidovaleric acid* $SO_2(NH \cdot [CH_2]_4 \cdot COOH)_2$, prepared by the oxidation of sulphonepiperidide with potassium permanganate, crystallises in small, colourless plates, and melts at 165°. The yield is 60 per cent. of the theoretical. The acid is hydrolysed by the action of water at 160°, and of hydrochloric acid at 100°. The *barium salt* melts at 246°, and, like the *copper salt*, which melts at 232°, is pulverulent; the *lead salt* crystallises in large, lustrous plates, melting at 198°. All these salts con-

tain $\frac{1}{2}$H$_2$O. The *methylic* and *ethylic salts* crystallise in large, lustrous plates melting at 81—82° and 69° respectively. The *anhydride* (*sulphonepiperidone*), $SO_2[N{<}^{CH_2 \cdot CH_2}_{CO \cdot CH_2}{>}CH_2]_2$, crystallises from ether in highly refractive prisms melting at 141°. J. B. T.

Technical Preparation of Cocaïne from Associated Alkaloïds. By C. LIEBERMANN (*Ber.*, **27**, 2051—2053).—The author anticipates a misconception to which the recent publication of Einhorn and Willstätter under this title (this vol., i, 478) might give rise. M. O. F.

Substitution Derivatives of Cocaïne. By A. EINHORN and H. HIS (*Ber.*, **27**, 1874—1879).—Derivatives of cocaïne, in which the substitution is in the benzoyl-group, may be prepared from ecgonine by converting it into the ether, and then acting on the latter with the anhydride or chloride of a substituted benzoic acid.

Orthochlorococaïne, $C_{10}H_{16}NO_3 \cdot CO \cdot C_6H_4Cl$, forms small, white crystals melting at 63—64°. The *platinochloride* crystallises in orange-coloured plates, and the *aurochloride*, in thin, yellow plates. The *hydriodide* crystallises from dilute alcohol in transparent lamellæ melting at 196—197°. *Orthochloro-d-cocaïne* is prepared from d-ecgonine, and forms compact white crystals. The *hydrochloride* which crystallises in thin, prismatic plates, melts and decomposes at 208°. The *platinochloride* melts at 210—211°, and the *aurochloride* at 152°. *Metanitrococaïne*, $C_{10}H_{16}NO_3 \cdot CO \cdot C_6H_4 \cdot NO_2$, is obtained by the direct nitration of cocaïne, and crystallises from alcohol in large, colourless prisms melting at 76—77°; when boiled with hydrochloric acid, it yields metanitrobenzoic acid. The *hydrochloride* forms prismatic needles; the *nitrate* melts at 164°; the *platinochloride* at 237°; and the *aurochloride* at 207·5—208°. *Metamidococaïne* is formed when the nitro-compound is reduced with tin and hydrochloric acid; it crystallises from alcohol in colourless, compact crystals, and melts at 125°. The *dihydrochloride* forms transparent, prismatic tablets, and melts at 227—228°, whilst the *dihydriodide* is a yellowish powder, and melts at 219°. *Metacocaïne-urethane*, $C_{10}H_{16}NO_3 \cdot CO \cdot C_6H_4 \cdot NH \cdot COOEt$, is obtained by the action of ethylic chlorocarbonate on amidococaïne. It crystallises from dilute alcohol in compact crystals melting at 143°. The *hydrochloride* is remarkably hygroscopic. *Metahydroxycocaïne*, which is prepared by diazotising a solution of amidococaïne hydrochloride, and boiling the liquid, crystallises from benzene in plates melting at 123°; it is soluble in aqueous soda, and is reprecipitated by carbonic anhydride. The *hydrochloride* forms dull, white, indistinct crystals; the *platinochloride* crystallises in well-developed, prismatic plates, and the *aurochloride* melts at 181—182°. A. H.

Substitution Derivatives of d-Cocaïne. By A. EINHORN and E. S. FAUST (*Ber.*, **27**, 1880—1887; compare foregoing Abstr.).— *Metanitro-d-cocaïne*, obtained by the direct nitration of d-cocaïne, is a colourless syrup. The *hydrochloride, hydrobromide, hydriodide*, and *nitrate* are all crystalline; the *platinochloride* melts at 232°; and the *aurochloride* at 163°. *Metamido-d-cocaïne* crystallises

from dilute alcohol in large, colourless, tetrahedral crystals, or in slender needles, and melts at 116—117°. The *dihydrochloride* melts at 208—209°, whilst the *aurochloride* melts and decomposes at 98°. *Metamido*-d-*cocaïne methiodide* melts at 197—198°. *Acetylamido*-d-*cocaïne* is obtained by the action of acetic chloride on the amido-compound; it forms small plates, and melts at 44—45°. The *hydrochloride* forms small plates, and melts at 196—197°. *Benzoylamido*-d-*cocaïne* is a colourless syrup, but yields a crystalline *hydrochloride*, which melts at 216—217°. *Metabenzenesulphonamide*-d-*cocaïne*,

$$C_{10}H_{16}NO_3 \cdot CO \cdot C_6H_4 \cdot NH \cdot SO_2Ph,$$
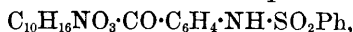
crystallises from dilute alcohol in small, yellowish plates, which melt at 69°.

d-*Cocaïne-urethane* is obtained as a colourless oil, which crystallises with great difficulty, forming prismatic needles melting at 100—101°. The *hydrochloride* melts at 214°. d-*Cocaïnecarbamide* is obtained by the action of potassium cyanate on the amido-compound, and forms small, scale-like crystals melting at 72°. The *hydrochloride* melts at 135°. d-*Cocaïnephenylthiocarbamide*, $C_{10}H_{16}NO_3 \cdot CO \cdot C_6H_4 \cdot NH \cdot CS \cdot NHPh$, is obtained by the direct union of the amido-compound with phenyl-thiocarbimide; it forms microscopic crystals, and melts at 190—193°. d-*Cocaïnethiocarbamide*, $(C_{10}H_{16}NO_3 \cdot CO \cdot C_6H_4 \cdot NH)_2CS$, is obtained by the action of carbon bisulphide on d-cocaïne as a fine, yellow powder, which melts at 63°. *Metahydroxy*-d-*cocaïne* crystallises from dilute alcohol in radially grouped prisms melting at 82°. The *hydrochloride* melts and decomposes at 201°. d-*Cocaïneazodimethylaniline*, prepared by adding dimethylaniline to a solution of diazo-d-cocaïne hydrochloride, crystallises from alcohol in brick-red plates, and melts at 220°. The *hydrochloride* forms a deep, bluish-violet coloured solution in water. d-*Cocaïneazodiphenylamine*, prepared in a similar manner, forms dark red plates melting at 172—173°. d-*Cocaïneazo-α-naphthylamine* forms red flakes, and could not be obtained in the crystalline state.   A. H.

Cytisine and Ulexine. By A. Partheil (*Arch. Pharm.*, 232, 161—177; compare Abstr., 1893, i, 119).—Attempts to invert cytisine failed. The crystallographical measurements of the nitrate, hydrobromide, and d-*tartrate*, $C_{11}H_{14}N_2O(CHOH \cdot COOH)_2 + 2H_2O$, prepared from cytisine and from ulexine respectively, confirm the identity of the two bases. These measurements, as well as those of cytisine hydriodide and methylcytisine platinochloride, are given in the paper.

The author has already shown that the apparent difference between the behaviour of cytisine and ulexine towards bromine, as interpreted by Magalhães (Abstr., 1891, 750) and by Gerrard and Symons (Abstr., 1890, 180; 1891, 334), is due to a misinterpretation of the latter chemists' analytical data. When bromine (50 grams) is added to an alcoholic solution of cytisine (5 grams), the precipitate which is at first formed redissolves, and an orange-yellow microcrystalline powder then separates. This is a *perbromide* of the formula

$$C_{11}H_{12}Br_2N_2O, HBr, Br_2 + \tfrac{1}{2}H_2O.$$

When this is digested with alcohol, the hydrobromide,

$$C_{11}H_{12}Br_2N_2O,HBr + \tfrac{1}{2}H_2O,$$

is obtained in colourless, silky needles which melt at 223°. By decomposing this hydrobromide with sodium hydroxide, *dibromocytisine*, $C_{11}H_{12}Br_2N_2O + 3H_2O$, is precipitated in gelatinous flocks. The boiling aqueous solution of the base becomes gelatinous as it cools. Ulexine behaves similarly towards bromine. *Dibromocytisine nitrate*, $C_{11}H_{12}Br_2N_2O,HNO_3$, prepared from the hydrobromide by means of silver nitrate, melts and decomposes at 196—197°. The *acetyl*-derivative, $C_{11}H_{11}AcN_2Br_2O$, crystallises in greenish-yellow needles melting at 164°. Dibromocytisine *platinochloride* and *aurochloride* are described.

Baryta water and moist silver oxide have no action on dibromocytisine; alcoholic potash in a sealed tube at 160—170° removes bromine from it, but the investigation of the action is not completed. Phosphorus pentachloride does not attack cytisine in chloroform solution.

By treating cytisine nitrate with fuming nitric acid, a *nitronitrosocytisine*, $NO \cdot C_{11}H_{12}N_2O \cdot NO_2$, is obtained in yellow crystals; it is soluble in boiling water and melts at 237°.   A. G. B.

Ptomaïne from Urine in a Case of Cancer. By A. B. GRIFFITHS (*Compt. rend.*, **118**, 1350—1351).—The urine of a patient suffering from cancer (*cancer uteri*) contained a ptomaïne *cancerine* of the composition $C_8H_5NO_5$. It crystallises in white microscopic needles, which dissolve in water and have an alkaline reaction. It forms a hydrochloride, platinochloride, and aurochloride, and gives a yellow precipitate with phosphotungstic acid, a brownish precipitate with phosphomolybdic acid, a red with silver nitrate, grey with mercuric chloride, and brownish precipitate with Nessler's reagent. It is very poisonous, and produces fever, and death in three hours.

C. H. B.

Peptone Salts of Egg-Albumin. By C. PAAL (*Ber.*, **27**, 1827—1851; compare Abstr., 1892, 895).—A number of peptone hydrochlorides have been prepared by the action of hydrochloric acid on egg-albumin under varying conditions of concentration, temperature, &c., fully described by the author. These salts are colourless, or pale-yellow, brittle, and amorphous, and are almost as hygroscopic as phosphoric anhydride; the latter property increases with the amount of combined acid. They are miscible with water in all proportions, dissolve readily in glacial acetic acid, more sparingly in phenol, and their solubility in the alcohols varies inversely with the molecular weight of the solvent, resembling the corresponding salts of the glutin-peptones in this respect. These compounds are not altered at 130°, have a sour, cheesy flavour, with a bitter aftertaste; they give the biuret, xanthoproteïn, and Millon's reactions, are incompletely precipitated from aqueous solution by phosphotungstic acid, and, in contrast to the glutin-peptone salts, yield soluble double salts with mercuric chloride. That they are true peptones is shown by the fact that little or no precipitate is produced with ammonium sulphate

or sodium chloride, and the subsequent addition of an acid or alkali causes no change. Although the salts in aqueous solution redden litmus paper, no free acid is present, as repeated evaporation of the liquid causes no change in the composition of the peptone. The chlorine is only partially removed by the addition of silver nitrate. Certain of the salts were found to yield small quantities of methyl- and ethyl-derivatives by treatment with the respective alcohols. In the salts of the albumin-peptones, as in those of the glutin-peptones, the quantity of acid present is in inverse proportion to the molecular weight.

The *free peptones* are prepared from the hydrochlorides by the action of silver sulphate in the manner previously described *(loc. cit.)*; the yield is 70—80 per cent. of the theoretical. They give the usual peptone reactions, are less hygroscopic than the salts, are sparingly soluble in methylic alcohol, and almost insoluble in ethylic alcohol. The *barium salts* are colourless and pulverulent, readily soluble in water, and somewhat hygroscopic. Zinc and copper salts produce no precipitate in solutions of the barium salt ; with ferrous sulphate, *ferrous peptonate* is obtained in solution, and gradually decomposes in presence of air into ferric hydroxide and peptone. *Silver peptonate* and *lead peptonate* are yellow, flocculent, insoluble precipitates, stable towards light. *Mercuric peptonate* is colourless, amorphous, and insoluble. Two *lead peptone sulphates* were also obtained ; they are somewhat hygroscopic ; the aqueous solution is pale, yellowish-brown, and is not decomposed by boiling.

Gastric juice converts albumin into peptones, and, as with hydrochloric acid, half the product consists of soluble (Hemi) peptones, half of insoluble (Anti) peptones ; these were further separated by dialysis, and in their general properties they resemble those described above.

A sample of commercial " albumin peptone " was found to consist almost entirely of albumoses, one of which is probably identical with Schrötter's alcohol soluble albumose.

Molecular weight determinations of the peptone salts and peptones by the cryoscopic and boiling point methods show that, exactly as in the case of the glutin derivatives, the percentage of acid increases as the molecular weight becomes smaller, and, as the molecular weights indicated by the first method were only half those deduced from the second, it follows that in the albumin-peptones also, one molecule of peptone is combined with one of hydrochloric acid. The molecular weight of the free peptones is about 400. The author concludes that the hydrolysis of the proteïds (peptonisation) can be followed, step by step, by the increasing proportions of acid, combined with the products characteristic of each phase of the reaction.   J. B. T.

Organic Chemistry.

Tautomerism. By J. W. BRÜHL (*Ber.*, **27**, 2378—2398, and *J. pr. Chem.* [2], **50**, 119—221).—See this vol., ii, 433.

Preparation of Bromoform. By P. FROMM (*Chem. Centr.*, 1894, i, 671—672; from *Pharm. Zeit.*, **39**, 164).—When calcium hypochlorite (3 mols.) and potassium bromide (6 mols.) are allowed to react with acetone (2 mols.), and the product distilled with steam, the yield of bromoform is only one-third of the theoretical, for the calcium hydroxide formed in the reaction decomposes some of the bromoform, forming calcium bromide, water, and carbonic oxide. The theoretical yield can be nearly attained by allowing the mixture to cool to 50°, adding an equal amount of calcium hypochlorite, and $\frac{3}{4}$ part of acetone, distilling with steam, and adding three times, at intervals, $\frac{1}{2}$ part acetone.

If for 1 mol. of acetone, 6 mols. of calcium hypochlorite, and 6 mols. of potassium bromide are taken, carbon tetrabromide is obtained in amount equal to 40—45 per cent. of the theoretical.　　C. F. B.

Bromine Derivatives of Tetrachlorethylene. By A. BESSON (*Compt. rend.*, **119**, 87—90).—When tetrachlorethylene is mixed with aluminium bromide in presence of an inert gas, and is gently heated, several bromochlorethylenes are obtained, and can be separated by distillation under low pressure.

Bromotrichlorethylene, C_2Cl_3Br, melts at $-12°$ to $-13°$, and boils at 145—148°; sp. gr. at 15° $= 2·02$. It is not attacked by bromine in the dark even at 100°, but in sunlight complete combination takes place with formation of $C_2Cl_3Br_3$, a white compound which sublimes at 100—125° under low pressure, and condenses in small prismatic crystals which melt and partially decompose at 178—180°; sp. gr. at 18° $= 2·44$.

Dibromodichlorethylene, $C_2Cl_2Br_2$, melts at 1—2°, and boils at 169—171°; sp. gr. at 15° $= 2·35$. Bourgoin has previously obtained a compound of the same composition by the action of aniline on $C_2Cl_4Br_2$ at 100°, and it is possible that the two compounds are isomeric, and have the constitutions $CCl_2{:}CBr_2$ and $CClBr{:}CClBr$ respectively. The compound $C_2Cl_2Br_2$ combines slowly with bromine under the influence of light, and yields a white solid, $C_2Cl_2Br_4$, which sublimes under low pressure at about 150°, and melts at 194—195°. Another compound, $C_2Cl_2Br_4$, melting at about 180°, has been described, and it is possible that the two are isomeric.

Ozonised oxygen combines slowly with dibromodichlorethylene, with formation of some carbonic chloride and liberation of bromine, which forms $C_2Cl_2Br_4$. The liquid has a disagreeable odour, and fumes on exposure to air; the fraction boiling at about 150° contains the compound $CClBr_2 \cdot COCl$, which yields the acid $CClBr_2 \cdot COOH$ when treated with water.

The product of the action of aluminium bromide on tetrachlorethylene also contains the compound C_2ClBr_3, already described by Demole.　　　　　　　　　　　　　　　　　　　　C. H. B.

Tribromacetonitrile. Some Derivatives of Polymeric Trichloracetonitrile. By C. BROCHE (*J. pr. Chem.* [2], **50**, 97—118; compare Abstr., 1893, i, 289).—Tribromacetamide is best made by carefully introducing aqueous ammonia under a layer of ethylic tribromacetate, and allowing the whole to remain for 12 hours at a temperature below 0°. Ethylic tribromacetate can be conveniently prepared by saturating an absolute alcoholic solution of tribromacetic acid with dry hydrogen chloride, the solution being cooled with ice and kept cool for 12 hours after complete saturation.

When concentrated aqueous ammonia is introduced under a layer of an ethereal solution of polymeric tribromacetonitrile, *diamidoperbromomethylcyanidine*, $CBr_3 \cdot C_3N_3(NH_2)_2$, is obtained; this forms white crystals, and does not melt below 300°. If the polymeric nitrile is shaken with dry ammonia gas in a flask that has been heated on the water bath, *amidodiperbromomethylcyanidine*, $C_3N_3(CBr_3)_2 \cdot NH_2$, is obtained; it forms white crystals, and melts and decomposes at 184—185°. When aqueous methylamine is introduced beneath an ethereal solution of the polymeric nitrile, *methylamidodiperbromomethylcyanidine*, $C_3N_3(CBr_3)_2 \cdot NHMe$, is formed; it melts at 192°. If an absolute alcoholic solution of the polymeric nitrile is heated on the water bath with excess of methylamine, then white *dimethyldiamidoperbromomethylcyanidine*, $CBr_3 \cdot C_3N_3(NHMe)_2$, melting at 263—264°, is formed. When aniline is introduced beneath a layer of an ethereal solution of the polymeric nitrile, yellow *anilinediperbromomethylcyanidine*, $C_3N_3(CBr_3)_2 \cdot NHPh$, melting at 205°, is obtained, whereas an alcoholic solution of the polymeric nitrile if heated with excess of aniline on the water bath, yields violet *dianilineperbromomethylcyanidine*, $CBr_3 \cdot C_3N_3(NHPh)_2$, melting at 280°. Polymeric trichloracetonitrile does not yield a derivative with aniline, nor does amidodiperchloromethylcyanidine, $NH_2 \cdot C_3N_3(CCl_3)_2$. The substances mentioned in this paragraph are, as a rule, easily decomposed by alkalis; bromoform and ammonium bromide are usually produced, and, if alcohol is present, a carbamine.

When phenylhydrazine is introduced beneath an ethereal solution of polymeric tribromacetonitrile, a substance, $C_{10}H_6N_5Br_3$, is formed, which crystallises in white needles and melts at 210°. It is possibly a triazole - derivative, with the constitution
$$CBr_3 \cdot \overset{\displaystyle N = C - NPh}{\underset{\displaystyle N - C - NH}{\underset{\displaystyle |}{C}} \quad \overset{\displaystyle N}{\underset{\displaystyle |}{}} \quad | \;} ;$$
aqueous potash decomposes it into phenylhydrazine and cyanuric acid. Under some circumstances, no such derivative is obtained, but only *phenylhydrazine hydrobromide*, N_2H_3Ph,HBr, melting at 204°. From polymeric trichloracetonitrile, no triazole derivative was obtained, but only phenylhydrazine hydrochloride, melting at 240°.

The action of nitrous acid on amidodiperbromomethylcyanidine results in a complete breaking down of the latter substance. The

same is usually the case with the corresponding chloro-derivative, but, if the reaction is carried out in chloroform solution, a substance, $C_5N_3Cl_5(OH)_2$, is obtained in slender, white needles, melting at 155°; it is soluble in alkalis, and yields a diethylic ether melting at 212°.

<div align="right">C. F. B.</div>

Synthesis of Unsaturated Alcohols. By G. WAGNER (*Ber.*, **27**, 2434—2439).—Unsaturated alcohols were obtained by adding a mixture of an aldehyde and allylic iodide to zinc shavings. When oxidised with permanganate, they yield glycerols and β-hydroxy-acids, together with some fatty acids, $R\cdot CHO + CH_2I\cdot CH\colon CH_2 \rightarrow$ $R\cdot CH(OH)\cdot CH_2\cdot CH\colon CH_2 \rightarrow R\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ $\rightarrow R\cdot CH(OH)\cdot CH_2\cdot COOH + CO_2$.

Acetaldehyde yields *methylallylcarbinol*, a liquid boiling at 115—116° under 750 mm. pressure, and with sp. gr. 0·852 at 0°/0°, 0·834 at 20°/0°. Its *acetate* boils at 133° under 743 mm. pressure, and has sp. gr. 0·911 at 0°/0°, 0·891 at 20°/0°. Both these compounds yield oily *dibromides.* The oxidation of the alcohol has already been described (Abstr., 1889, 231).

Valeraldehyde yields *isobutylallylcarbinol,* boiling at 162—163° under 748 mm. pressure, and with sp. gr. 0·854 at 0°/0°, 0·834 at 21°/0°; the *acetate* boils at 178·5—179·5° under 760 mm. pressure, and has sp. gr. 0·889 at 0°/0°, 0·871 at 20·5°/0°. When oxidised, the alcohol yields the *glycerol,* which melts at 50°, and *hydroxyisoamyl-acetic acid* (a liquid, the calcium salt of which crystallises with H_2O), together with isovaleric and formic acids.

Œnanthaldehyde yields *hexylallylcarbinol,* boiling at 211—212° under 751 mm. pressure, and having sp. gr. 0·850 at 0°/0°; the *acetate* boils at 224—225° under 738·7 mm. pressure. When oxidised, the alcohol yields the *glycerol,* melting at 78°, β-*hydroxynonic acid,* melting at 48—51°, and œnanthylic acid.

Oxymethylene yields, though less easily, *allylcarbinol* itself. This is a liquid which boils at 113·5° under 748 mm. pressure ; its *dibromide* has sp. gr. 1·976 at 0°/0°, and boils at 131—141° under 16 mm. pressure. The *acetate* boils at 125° under 750 mm. pressure, and has sp. gr. 0·934 at 0°/0°; its *dibromide* boils at 143—144° under 23 mm. pressure, and has sp. gr. 1·762 at 0°/0°. When oxidised, the alcohol yields the *glycerol* and formic acid; the former boils at 190—191° under 18 mm. pressure, and yields a *triacetate,* which boils at 163—164° under 17 mm. pressure, and has sp. gr. 1·155 at 0°/0°. When oxidised under fitting circumstances, this glycerol appears to yield a lactone, $O{<}{\begin{smallmatrix}CH_2\cdot CH\cdot OH\\ CO\cdot CH_2\end{smallmatrix}}$, and in this respect differs from the other glycerols mentioned, which do not, like it, contain a second $CH_2\cdot OH$ group.

<div align="right">C. F. B.</div>

Formation of Succinic acid and Glycerol in Alcoholic Fermentation. By J. EFFRONT (*Compt. rend.,* **119**, 92—93).—Glycerol and succinic acid, although always amongst the products of alcoholic fermentation, are not always present in the same ratio. The proportion of these secondary products is small at the commencement

of fermentation, but increases towards the end. Determinations of the quantities of glycerol and succinic acid in worts fermented by yeast accustomed to fluorides gave the following results per 100 grams of sugar decomposed :—

	24 hrs.	48 hrs.	72 hrs.	96 hrs.
Glycerol	0·1503	0·3508	0·3992	0·81
Succinic acid	0·02541	0·04755	0·06759	0·0924

The maximum quantities of glycerol and succinic acid are found when the power of the yeast is almost exhausted owing to the disappearance of the fermentable substances. It would seem, therefore, that the formation of these products is due to an enfeebled condition of the yeast, and yeasts accustomed to fluorides and with increased fermenting power (this vol., ii, 425) are towards the end of the process in much the same condition as ordinary yeast at the commencement of ordinary fermentation.   C. H. B.

Levoglucosan. By TANRET (*Compt. rend.*, **119**, 158—161).—When picein (this vol., i, 616) is heated in sealed tubes at 100° with 20 times its weight of barium hydroxide solution for four hours, it is converted into levoglucosan, which, after precipitation of the barium, removal of the piceol by means of ether, and concentration of the liquid to a syrup, is extracted by means of boiling ethylic acetate, and finally crystallised from water.

Coniferin and salicin also yield glucosans under similar conditions, but a much more concentrated barium hydroxide solution is required, from 30 to 40 hours' ebullition is necessary, and the products are difficult to purify.

Levoglucosan has the composition $C_6H_{10}O_5$, and cryometric determinations show that the molecular weight is 162. It forms, large, rhombic crystals (1·0164 : 1 : 0·5674), very soluble in water and alcohol, and slightly soluble in ether ; sp. gr. = 1·59. When heated at 178°, it melts, and under low pressure at this temperature, it sublimes without decomposing. Its rotatory power is $[\alpha]_D = -66·5°$ in a 10 per cent. aqueous solution, $[\alpha]_D = -81·5°$ in a 50 per cent. aqueous solution, $[\alpha]_D = -70·5°$ in an alcoholic solution, $[\alpha]_D = -77·5°$ in a solution in ethylic acetate. The rotatory power shows no appreciable variation with either time or temperature.

Levoglucosan yields ordinary glucose when heated for some time with dilute acids. It does not reduce Fehling's solution, and is not fermented by beer yeast; it is not affected by emulsin, and is not precipitated by basic lead acetate nor ammoniacal lead acetate.

The *benzoyl*-derivative, $C_6H_4O_2(OBz)_3$, is obtained by the action of benzoic chloride in presence of sodium hydroxide solution, and is a white powder, which melts at 194°, and is only very slightly soluble in water, alcohol, or ether. The *acetyl*-derivative, $C_6H_4O_2(OAc)_3$, is obtained by the action of acetic anhydride in presence of a small quantity of zinc chloride, and crystallises in needles melting at 107—108°. In alcoholic solution, its rotatory power is $[\alpha]_D = -45·5°$. It would seem from these results that glucosan behaves as a trihydric alcohol, but this conclusion is not yet definitely established.

C. H. B.

Synthetic Glucosides. By E. FISCHER and L. BEENSCH (*Ber.*, **27**, 2478—2486).—The synthetic glucosides described in this paper were prepared by the method already made known (this vol., i, 3).

Ethylglucoside, $C_6H_{11}EtO_6$, has now been obtained in the crystalline condition; the method is, however, somewhat lengthy and complicated. When pure, it crystallises in mammelated groups of colourless needles, and melts at 65°. An aqueous solution containing 9·47 per cent. was found to have a sp. gr. of 1·024, and a specific rotatory power at 20° $[\alpha]_D = +140·2°$; birotation was not observed. It does not reduce Fehling's solution when boiled with it for a short time, and is hydrolysed with tolerable rapidity when warmed with acids, somewhat more slowly, however, by invertase at 50°. The behaviour towards yeast has already been described by Fischer and Thierfelder (this vol., i, 487).

Methylgalactoside, $C_6H_{11}MeO_6$, crystallises in delicate needles containing 1 mol. H_2O; it has a sweet taste, is sparingly soluble in cold alcohol, and the anhydrous compound melts at 111—112°. An aqueous solution containing 9·92 per cent. has a sp. gr. of 1·0296, and a specific rotatory power $[\alpha]_D + 163·4°$: birotation was not observed; it only reduces Fehling's solution when boiled therewith for a protracted period, is readily hydrolysed by dilute acids, but apparently not by invertase; it is not fermented by Frohberg yeast.

Ethylgalactoside, $C_6H_{11}EtO_6$, forms colourless needles, melts at 138—139° (corr.), remains unaltered when treated with invertase or with Frohberg yeast, and has a specific rotatory power $[\alpha]_D = +178·75°$.

Benzylarabinoside, $CH_2Ph·C_5H_9O_5$, crystallises in colourless needles, melts at 172—173° (corr.), has a faint bitter taste, is readily hydrolysed by acid but not by invertase, and is not fermented by Frohberg yeast. An aqueous solution containing 1·03 per cent. had a specific rotatory power $[\alpha]_D = +215·2°$.

Propylglucoside and *glycerylglucoside* (from glycerol and glucose) were only obtained in the amorphous condition.

Glucosidogluconic acid, $C_{12}H_{22}O_{12}$, is obtained by the interaction of glucose and gluconic acid, under the influence of hydrogen chloride, as an amorphous powder, consisting of a mixture of the acid and the lactone; it was isolated by a complicated process. An aqueous solution of this product was precipitated by basic lead acetate and basic lead nitrate. The salts are readily soluble in water and amorphous; the calcium salt was analysed. When the acid is warmed on the water bath with 5 per cent. sulphuric acid, it is hydrolysed, yielding glucose and gluconic acid. The calcium salt was found not to ferment with Frohberg yeast, and to be unattacked by invertase. The authors consider that the acid is either a structural isomeride or a stereoisomeride of maltobionic acid; they have not succeeded in transforming the acid or its lactone into the corresponding sugar, which they conjectured might possibly turn out to be identical with isomaltose (Fischer, Abstr., 1891, 412).

Galactosidogluconic acid, *arabinosidogluconic acid*, *glucosidoglycollic acid*, and glucosidoglyceric acid were also prepared.

A. R. L.

Some Osazones and Hydrazones of the Sugar Group. By E. Fischer (*Ber.*, **27**, 2486—2492).—When natural xylose is reduced by sodium amalgam, it yields a polyhydric alcohol, xylitol, which is optically inactive by intramolecular compensation; this substance was isolated in the form of a colourless syrup, containing only traces of ash constituents. If the latter is oxidised with bromine and soda, and the product (*i-xylose*) is treated with phenylhydrazine acetate in the usual manner, *i*-xylosazone, $C_{17}H_{20}N_4O_3$, is obtained : it crystallises in delicate, yellow needles, melts and decomposes at 210—215°, and its solution in glacial acetic acid is optically inactive.

According to Alechin (Abstr., 1890, 733), melezitose decomposes on partial hydrolysis into glucose and turanose; an analysis of the amorphous sodium derivative of the latter by Alechin indicated that the sugar has the formula $C_{12}H_{22}O_{11}$. The author having been furnished with a specimen of turanose, prepared the osazone, which gave values on analysis agreeing with the formula $C_{12}H_{20}O_9(N_2HPh)_2$. It crystallises from hot water in nodular aggregates of very minute needles, which separate in a form resembling a jelly and are extremely like isomaltosazone; the pure compound melts and decomposes at 215—220°. Alechin's formula for turanose is therefore confirmed.

Arabinose parabromophenylhydrazone, $C_5H_{10}O_4\cdot N_2H\cdot C_6H_4Br$ (compare Abstr., 1892, 439), is obtained by mixing aqueous solutions of parabromophenylhydrazine acetate and arabinose; it melts at 165° (corr.) and dissolves in about 40 parts of water. The formation of this hydrazone may be used as a test for the presence of arabinose, the reagents used being a freshly prepared solution of parabromophenylhydrazine in 3·5 parts of 50 per cent. acetic acid and 12 parts of water, and a 1 per cent. solution of arabinose ; these solutions are mixed in the proportions of 1 part of sugar to 2 parts of parabromophenylhydrazine. In this way, arabinose may be detected in presence of xylose. The parabromophenylhydrazine acetate solution must not be heated, on account of the ease with which the acetyl-derivative is formed.

Wohl (Abstr., 1893, i, 294) found a value for the melting point of *i*-arabinosazone somewhat higher than that observed by the author (*ibid.*, 292), who, having now subjected this osazone to repeated recrystallisation from hot water, finds the melting point to be 169—170° (corr.). A. R. L.

Action of Acids on Glycogen. By M. Cremer (*Zeit. Biol.*, **31**, 181—182).—Glycogen was heated with oxalic acid ; glucose and isomaltose (identified as their osazones) were found in the product, the isomaltose corresponding with 10 per cent. of the glycogen. Maltose was never obtained, and the opinion is expressed that in those cases in which maltose has been described as occurring after the action of acids or ferments on starch and glycogen, it has arisen secondarily from isomaltose. W. D. H.

Action of Ferments and Cells on Sugars. By M. Cremer (*Zeit. Biol.*, **31**, 183—190).—In view of recent discoveries relating to the carbohydrates, the paper discusses, with references to authors, the

possibility of ferments and living cells bringing about the conversion of one kind of sugar into another, and also the relationship of the carbohydrate groups. Special stress is laid on yeast-glycogen (a starch-like substance coloured brown by iodine), which is formed in the yeast cell after feeding on solutions of dextrose, cane sugar, or levulose. The hypothesis is advanced that the levulose is first changed into dextrose. W. D. H.

Constitution of Iodide of Starch. By C. LONNES (*Zeit. anal. Chem.*, **35**, 409—436).—See this vol., ii, 475.

Substitution of Alkyl Radicles in Union with Carbon and Nitrogen. By C. MATIGNON (*Compt. rend.*, **119**, 78—79; and by BERTHELOT, *ibid.*, 79—80).—A question of priority. C. H. B.

Derivatives of Propylamine. By F. CHANCEL (*Compt. rend.*, **119**, 233—235).—*Propylpropylidenamine*, $C_3H_6:N\cdot C_3H_7$, is readily obtained by the action of propaldehyde on propylamine. It is a colourless, mobile liquid with a very disagreeable ammoniacal odour; it boils at 102° under a pressure of 760 mm., and is only slightly soluble in water; sp. gr. at 0° = 0·84. The salts of this amine cannot be prepared because, in presence of acids, it regenerates propaldehyde and propylamine.

Propylacetamide, $CH_3\cdot CO\cdot NHPr$, is obtained by the action of acetic chloride on propylamine in presence of dry ether, or more conveniently by the action of ethylic acetate on propylamine in sealed tubes at 140—150°. It is a colourless, somewhat syrupy liquid with a feeble odour, and boils without decomposing at 222—225° under ordinary pressure.

Dipropylacetamide, $CH_3CO\cdot NPr_2$, is obtained by the action of acetic chloride on dipropylamine in presence of ether, but cannot be obtained from ethylic acetate even at 160°. It boils at 209—210°.

Tetrapropylcarbamide, $CO(NPr_2)_2$, is obtained by the action of carbonic chloride on dipropylamine in presence of benzene. The action is very energetic, and it is desirable to use a slight excess of dipropylamine, and to heat for a short time towards the end in order to prevent the formation of dipropylcarbamine chloride. Tetrapropylcarbamide is a somewhat syrupy liquid, with a burning taste, and an aromatic odour recalling that of menthol. It boils without decomposing at 258° under a pressure of 755 mm., and is insoluble in water, but soluble in alcohol and benzene; sp. gr. at 0° = 0·905°. C. H. B.

Sulphur Derivatives of Propylamine. By M. LEHMANN (*Ber.*, **27**, 2172—2177).—*Diphthalimidopropylic bisulphide*,

$$S_2(CH_2\cdot CH_2\cdot CH_2\cdot N:C_8H_4O_2)_2,$$
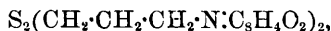
which melts at 90—91°, is obtained by oxidising propylmercaptophthalimide with iodine. When heated with hydrochloric acid at 180°, it yields the hydrochloride of diamidopropylic bisulphide; the *dibenzoyl-* derivative of this base forms colourless needles melting at 122°. When the latter substance is heated with phosphorus pentachloride, it yields mesophenylpenthiazoline (Abstr., 1893, i, 427). *Phthalyl-*

homotaurine, $C_8H_4O_2$:$N\cdot CH_2\cdot CH_2\cdot CH_2\cdot SO_3H$ + $1\frac{1}{2}H_2O$, is formed when nitric acid is employed for the oxidation of propylmercaptophthalimide instead of iodine.

Diphthalimidopropylic sulphide, $S(CH_2\cdot CH_2\cdot CH_2\cdot N$:$C_8H_4O_2)_2$, melting at 118°, is obtained by the combined action of bromine and bromopropylphthalimide on propylmercaptophthalimide in alcoholic solution. The free base, *thiopropylamine* $(NH_2\cdot CH_2\cdot CH_2\cdot CH_2)_2S$, is a colourless oil which boils at 247—248° (753 mm.). On oxidising the sulphide with bromine, *diphthalimidopropylsulphoxide* is formed; it crystallises in needles which melt at 158—159°, and under the influence of hydrochloric acid yields the hydrochloride of *diamidopropylsulphoxide*; the picrate melts at 208°. If the sulphide is oxidised with chromic acid, *diphthalimidopropylsulphone*,

$$SO_2(CH_2\cdot CH_2\cdot CH_2\cdot N$:$C_6H_4O_2)_2,$$
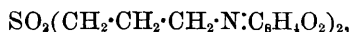
is obtained, separating from nitrobenzene in colourless plates which melt at 173°; the action of alcoholic potash results in the formation of *propylsulphonediphthalamic acid*,

$$SO_2(CH_2\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot COOH)_2.$$
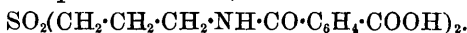
The acid melts at 181—186°, and yields *diamidopropylsulphone hydrochloride*, with elimination of phthalic acid; this salt melts at 203—206°, and the picrate forms orange needles which melt at 192—197°.

Diphthalimidoethylpropylic sulphide is prepared by acting on propylmercaptophthalimide with bromethylphthalimide and bromine in alcoholic solution; it forms colourless needles which melt at 123—124°.

ω-Amidopropylpiperidine, $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot C_5NH_{10}$, a colourless liquid boiling at 204° (751 mm.), is obtained by the interaction of bromopropylphthalimide and piperidine; the *picrate* forms golden-yellow prisms which melt at 209°. M. O. F.

Octomethylenediamine. By M. VAN BREUKELEVEEN (*Rec. Trav. Chim.*, **13**, 34—35).—*Octomethylenediamine*, $NH_2\cdot[CH_2]_8\cdot NH_2$, is readily obtained by the action of an alkaline solution of sodium hypobromite on sebacamide (Abstr., 1892, 1180), and is separated by extracting with ether, evaporating the ethereal solution, and subjecting the residue to fractional distillation. It melts at 50—52°, boils at 236—240° (uncorr.), and attracts carbonic anhydride rapidly from the atmosphere. The *platinochloride* is crystalline, and, on heating, commences to blacken at 230°. H. G. C.

Ethanehydrazoethane. By C. D. HARRIES (*Ber.*, **27**, 2276—2282).—When diformylhydrazine, obtained by warming hydrazine hydrate with formic acid, is treated with alcoholic soda in aqueous solution, it yields a mono- and a disodium salt. The former crystallises in slender, interlacing needles, the latter in long needles. Both salts are alkaline to turmeric, reduce Fehling's solution, and with warm water yield free hydrazine and sodium formate. The *lead salt*, $C_2H_2O_2N_2Pb$, is obtained by adding basic lead acetate to a solution of either of the sodium salts; it is an amorphous, white precipitate, reduces Fehling's solution when warmed with it, and is scarcely altered by prolonged boiling with water.

Diformylethanehydrazoethane, CHO·NEt·NEt·CHO, is obtained by heating the lead salt dried at 105° with sand, magnesium oxide, and ethylic iodide in a sealed tube for 20 hours at 110°. It is a viscid oil, boils at 120—130° under 20 mm. pressure, is volatile with steam, and reduces Fehling's solution slowly when boiled with it. Besides this compound, diformylethylhydrazine is also formed during the reaction, and the residue, after treatment with strong potassium hydroxide, yields ethanehydrazoethane and ethylhydrazine.

Ethanehydrazoethane, NHEt·NHEt, is obtained by heating the preceding compound with fuming hydrochloric acid, and then treating the cold solution with hydrogen chloride; the filtrate, when mixed with alkali and distilled, yields pure ethanehydrazoethane. This boils at 84—86° under 758 mm. pressure, is a colourless, limpid, highly refractive liquid, has an ethereal and ammoniacal odour, and reduces Fehling's solution and silver nitrate. It closely resembles ethylhydrazine. The *hydrochloride* crystallises in beautiful plates, and melts at 160°. When heated with strong hydrochloric acid at 150—160°, it yields ammonium chloride and ethylic chloride. When treated with red mercuric oxide in aqueous solution, a strong smell of mercurydiethyl is observed, and on adding solid potash, a small quantity of an oil is precipitated; this boils at 65—70°, does not reduce Fehling s solution, and quickly reduces silver and mercury solutions; on analysis, it gave numbers which did not agree very well with the formula NEt·NEt. When treated with sodium nitrite in hydrochloric acid solution, it yields ethylic nitrite and a small quantity of liquid which boils at 150°, has the properties of a nitroso-compound, but does not reduce Fehling's solution.   E. C. R.

Direct Formation of β-Alkylhydroxylamines. By C. A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, **13**, 46—49).—The β-alkyl derivatives of hydroxylamine may be readily obtained by boiling an aqueous solution of hydroxylamine with an alkylic iodide and a little methylic alcohol, the hydriodide of the base separating out in crystals, which, after washing with alcoholic ether, are quite pure. The *hydriodides* of *β-methylhydroxylamine*, NHMe·OH, and of *β-ethylhydroxylamine*, NHEt·OH, have been prepared in this manner; they are not altered at 200°, and do not reduce silver nitrate, but at once decolorise Fehling's solution in the cold. The free β-hydroxylamines have been recently obtained by Kjellin, and the author has therefore not made any further experiments in this direction.

For the preparation of the β-alkyl-derivatives, it is not necessary to prepare pure hydroxylamine; a suitable solution is obtained by adding the equivalent quantity of strong potash to a concentrated solution of hydroxylamine hydrochloride, mixing with an equal bulk of alcohol, and filtering from the precipitated potassium chloride.
H. G. C.

Mesoxalic acid and Bismuth Mesoxalate. By H. CAUSSE (*Compt. rend.*, **119**, 228—231).—The oxidation of glycerol becomes less violent in presence of bismuth nitrate, or some other metallic salt capable of forming insoluble compounds with the products of oxidation.

100 c.c. of nitric acid of sp. gr. 1·39 is mixed with 250 c.c. of a saturated solution of potassium nitrate, and the mixture is saturated with basic bismuth nitrate, and afterwards heated at 50° for half an hour in presence of excess of this salt. The filtered liquid is mixed with one-third its weight of glycerol of 30° B., and the mixture is distributed in quantities of 75 c.c. in flasks of 150 c.c. capacity. The flasks are gently heated until evolution of gas begins, and are then removed from the flame. The oxidation at first proceeds slowly, but eventually becomes very violent. When the liquid cools, brilliant white crystals separate, and are collected and washed with cold distilled water. This product is *basic bismuth mesoxalate*, C_3HO_6Bi; it crystallises in microscopic, rhomboidal plates which become yellow at 50—60°, and carbonise if the heating is prolonged. The salt has the general properties of bismuth salts, and is decomposed by hot water. Acids and alkalis decompose it, especially on heating, and the mesoxalic acid is destroyed. Acetic anhydride in sealed tubes at 100° dissolves the salt without decomposing it, and it separates unchanged when the liquid cools.

If the bismuth mesoxalate is suspended in water containing some potassium hydrogen carbonate, and treated with hydrogen sulphide, it yields mesoxalic acid, which can be recognised by the formation of its barium and silver salts, its action on Fehling's solution, and the formation of its compound with phenylhydrazine.

Potassium hydrogen mesoxalate, $C_3H_3O_6K + 2H_2O$, forms very deliquescent crystals; it has a strongly acid taste, and dissolves in water, but is insoluble in alcohol and in ether. *Potassium antimony mesoxalate*, $C_3H_2(SbO)KO_6 + H_2O$, is obtained by boiling the preceding salt with antimony oxide; it forms microscopic prisms grouped in rosettes.   C. H. B.

Bromomesaconic acid. By A. MICHAEL and G. TISSOT (*Ber.*, **27**, 2130).—The authors have prepared bromomesaconic acid in the same manner as Lossen and Gerlach (this vol., i, 441), and have examined the properties of the acid and its salts. Their results confirm those of Lossen and Gerlach, except with regard to the amount of water of crystallisation of the calcium salt, which they find to be $2H_2O$ instead of $1H_2O$.   H. G. C.

Preparation of Glutaric acid. By E. KNOEVENAGEL (*Ber.*, **27**, 2345—2346).—It has been observed that primary and secondary amines induce the condensation of aldehydes with ethylic acetoacetate and ethylic sodiomalonate. When the latter is brought in contact with formaldehyde and a small quantity of diethylamine or piperidine, tetrethylic methylenedimalonate is formed; from this, glutaric acid may be obtained by heating it for six hours with aqueous hydrochloric acid.   M. O. F.

Oxamidedioxime. By A. F. HOLLEMAN (*Rec. Trav. Chim.*, **13**, 80—87).—Oxamidedioxime, on oxidation with potassium ferricyanide in alkaline solution, yields ammonia, carbonic anhydride, and

nitrogen. By the action of bromine water on oxamidedioxime, a sparingly soluble crystalline compound is obtained in small quantity; it dissolves in alkalis, and the solution does not contain oxalic acid. *Oxamidedioxime nitrate*, $C_2(NOH)_2(NH_2)_2,2HNO_3$, is prepared by the action of dilute nitric acid (1 : 4) on the oxime; it crystallises in rhombic plates, and explodes at 72°. The compound is only stable when pure; by the further action of nitric acid, it is converted into nitrogen and carbonic anhydride. Oxamide and nitrous oxide are formed by the interaction of nitrous acid and oxamidedioxime. *Dibenzoyloxamidedioxime*, $NH_2 \cdot C(NOBz) \cdot C(NH_2):NOBz$, crystallises from glacial acetic acid in long needles melting at 222°; it is insoluble in alkalis and mineral acids, with the exception of concentrated sulphuric acid, which converts it into benzoic acid, and it is not affected by bromine at ordinary temperatures. *Oximamidoxalic acid*, $NH_2 \cdot C(NOH) \cdot COOH$, is formed, together with oxalic acid, ammonium chloride, and hydroxylamine hydrochloride, by the action of hydrochloric acid on oxamidedioxime, it decomposes violently at 158°, gives the reactions of the amidoximes, and, by the further action of hydrochloric acid, is converted into oxalic acid. The *silver salt* is explosive. *Oxamidedioxime picrate*, $C_2H_6N_4O_2,C_6H_3N_3O_7$, is deposited from water in orange-yellow crystals melting at 127°. The *phosphate*, $C_2H_6N_4O_2,H_3PO_4$, crystallises with difficulty in stellate needles, and decomposes at 70—80°.

Succinamidedioxime picrate, $C_2H_4 \cdot [C(NH_2):NOH]_2,2C_6H_3N_3O_7$, crystallises in long, yellow needles melting at 197°. The *phosphate*, $C_4H_{10}N_4O_2,2H_3PO_4$, is deposited in hygroscopic plates, decomposing at 133°. Attempts to prepare the silver salts of the two amide-dioximes were not very successful; the oxalate appears to exist, but is very unstable; succinamidedioxime reduces silver solutions.

<div align="right">J. B. T.</div>

Amido-acids obtained by the Breaking Down of Vegetable Proteïds.

By E. FLEURENT (*Compt. rend.*, **119**, 231—233).—When aspartic acid is heated with barium hydroxide solution under pressure, it is converted into oxalic, succinic, and acetic acids and ammonia; the conversion of the nitrogen into ammonia being complete only with an excess of barium hydroxide and under a somewhat high temperature, and after heating for many hours.

With glutamic acid, even after prolonged heating, only a small proportion of the nitrogen is converted into ammonia, and neither carbonic nor oxalic acid is formed.

It would seem that the differences observed between the decomposition of vegetable proteïds and of animal proteïds under the influence of barium hydroxide solution (this vol., i, 214) may be attributed to the intermediate formation of aspartic and glutamic acids, which afterwards decompose in a manner peculiar to themselves, the ratios being disturbed by the production of oxalic acid, and not carbonic acid as was previously supposed (*loc. cit.*). It would also seem that the constitution usually attributed to aspartic acid and analogous compounds requires reconsideration.

<div align="right">C. H. B.</div>

Furalcyanacrylic acid and its Derivatives. By R. Heuck ʻ(*Ber.*, **27**, 2624—2626).—*Furalcyanacrylic acid,*

$$C_4OH_3 \cdot CH{:}C(CN) \cdot COOH,$$
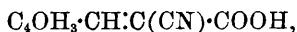
is prepared by heating molecular proportions of furfuraldehyde and cyanacetic acid at 160° for half an hour; it crystallises from dilute alcohol in yellow needles, and melts at 218°. The *ethylic* salt is formed when a mixture of ethylic cyanate, furfuraldehyde, and acetic anhydride is heated at 180° for several hours (compare Carrick, Abstr., 1892, 1086; Fiquet, Abstr., 1893, i, 455). A more convenient method is to heat furfuraldehyde and ethylic cyanacetate for a few minutes with sodium dissolved in a small quantity of alcohol. Recrystallised from alcohol, it forms colourless needles melting at 94°, and boiling at 295—300°, undergoing partial decomposition. Addition of alcoholic potash to the cold solution develops a brilliant, blue coloration, rapidly changing to reddish-violet, and finally becoming brown. The *acetyl* derivative forms colourless needles which melt at 87°, resolidify at 90—95°, and again fuse at 160°.

The free acid loses carbonic anhydride at 220°, and an oil can be separated by distillation, having an odour suggestive of cinnamene, and consisting probably of furalcyanethylene. M. O. F.

Colour Reactions of certain Sulphur Compounds which occur with Aniline Bases. By A. Hantzsch and H. Freese (*Ber.*, **27**, 2529—2534).—The authors have failed to obtain the condensation products of paramidophenol and acetone or methyl ethyl ketone described by Haegele (Abstr., 1892, 1451); the sole product was pure paramidophenol, which melted at 183°, was stable in air, and gave no coloration with calcium hypochlorite. Corresponding experiments with aniline gave a similar result. Specimens of commercial paramidophenol and aniline were found to contain 0·2 and 0·04 per cent. of sulphur respectively. Attempts to isolate the sulphur compound from aniline have not yet been successful, but, from its behaviour, there is little doubt that it is amidothiophen. The fractional crystallisation of aniline sulphate causes the thiophen-derivative to accumulate in the latter portions; it was converted into a *platinochloride*; the crystals of this are darker, and have a slightly different habit from those of aniline platinochloride, but the quantity obtained was very small. The more sparingly soluble aniline sulphate gave only a slight coloration with calcium hypochlorite. With aniline hydrochloride, the separation is less complete, and the thiophen-derivative accumulates in the first fractions.

Acetanilide, which melts at 115—116°, becomes brown, but is not hydrolysed by the action of concentrated sulphuric acid at 100°; the aniline obtained by hydrolysis of the residue with hydrochloric acid is almost pure.

An incomplete separation of aniline and amidothiophen is accomplished by fractional distillation, either alone or in a current of steam; the first fractions of the aniline are the purer.

The best method for the purification of aniline consists in boiling it for some time with acetone.

It is interesting to contrast these observations with those of V. Meyer, which led him to the discovery of thiophen in benzene.

J. B. T.

Aromatic Nitro-derivatives. **Dinitrobenzenes.** By C. A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, **13**, 101—147).—The separation of orthodinitrobenzene from the residue obtained during the manufacture of metadinitrobenzene has been previously described (Abstr., 1893, i, 256). A detailed account of the preparation of paradinitrobenzene from quinonedioxime by Nietzki and Guitermann's method (*Ber.*, **21**, 428) is given; the yield is 50—55 per cent. of the oxime. At 18°, the sp. gr. of metadinitrobenzene is 1·575, of orthodinitrobenzene, 1·59, and of paradinitrobenzene, 1·625; the sp. gr. increases therefore as the melting point rises. The boiling points of the three isomerides have been determined under various pressures, the ortho-derivative boils at 319° (773·5 mm.), the meta-compound at 302·8° (770·5 mm.); the para-compound at 299° (777 mm.), under 20—21 mm. pressure its boiling and melting points are identical, 172·1°. The solubility of the compounds in the following liquids has been determined—methylic, ethylic, and propylic alcohols, carbon bisulphide, benzene, ethylic acetate, toluene, carbon tetrachloride, and water; the results verify Carnelley and Thomson's rule that the solubility of isomeric compounds decreases as the melting points rise. Contrary to the statement in Beilstein's *Handbuch*, all three isomerides are volatile with steam, but under similar conditions about four times as much of the meta-compound volatilises as of the ortho-derivative, the para-compound is intermediate in this respect. Metadinitrobenzene is converted by the action of soda into metadinitroazoxybenzene, ammonia, nitrous acid, oxalic acid, and in small quantity, a brown, amorphous acid, which was not further investigated. Paradinitrobenzene, contrary to the statement of Hepp. is converted into paranitrophenol and nitrous acid by heating with soda (5—10 per cent.) during 3—6 hours; the yield is 75—80 per cent. of the theoretical. With more concentrated soda, the reaction is complex and the yield of nitrophenol smaller. *Paradinitroazoxybenzene* is formed in very small quantity along with the phenol; it crystallises in orange-red needles, and melts at 211°. By the action of ethylic alcoholic soda on metadinitrobenzene, dinitroazoxybenzene is readily formed; Michler and Klinger stated that this change was only accomplished in methylic alcoholic solution. Paradinitrobenzene resembles the ortho-compound in its behaviour towards alcoholic soda, one nitro-group being displaced by ethoxyl or methoxyl; the same change is produced by heating the dinitrobenzene with alcohol alone at 250°. *Paranitromethoxybenzene* and *paranitroethoxybenzene* melt at 52° and 58° respectively; both are crystalline. Metadinitrobenzene is not acted on by methylic alcoholic ammonia at 250°. Paradinitrobenzene is converted into a mixture of paranitraniline and paranitromethoxybenzene or paranitroethoxybenzene by heating with methylic or ethylic alcoholic ammonia above 150°, but below this temperature no change occurs. From the author's experiments, it appears that the presence of ammonia lowers, by about 100°, the temperature at which the substitution of the group OMe for

NO$_2$ takes place, and this temperature is only slightly below that at which the substitution of NH$_2$ for NO$_2$ occurs, a small increase in the temperature therefore causes the reverse change. Laubenheimer has shown that orthonitraniline is formed quantitively from orthodinitrobenzene and alcoholic ammonia at 100°.

The action of chlorine and bromine on the three dinitrobenzenes has been previously described (Abstr., 1892, 305). With iodine, at a temperature of 300—330°, the dinitrobenzenes yield iodonitrobenzenes. The higher the atomic weight of the halogen, the less readily does it act on the dinitrobenzenes. J. B. T.

Trinitrobenzene and 1 : 3 : 5-Dinitrophenol. By C. A. LOBRY DE BRUYN and F. H. VAN LEENT (*Rec. Trav. Chim.*, **13**, 148—154).—The trinitrobenzenes, 1 : 3 : 5 (m. p. 122°) and 1 : 2 : 4 (m. p. 57·5°), accord with Carnelley and Thomson's rule. Their solubility in the following liquids has been determined: benzene, chloroform, methylic alcohol, ethylic alcohol, ether, and carbon bisulphide (compare preceding abstract). Tetranitroazoxybenzene and 1 : 3 : 5-*dinitrophenol* are formed by boiling 1 : 3 : 5-trinitrobenzene with sodium carbonate or soda. With alcoholic soda at ordinary temperatures, 1 : 3 : 5-*dinitroethoxybenzene* is obtained, and crystallises in yellow needles melting at 90°. Alcoholic ammonia gives a brownish-red coloration with symmetrical trinitrobenzene; on evaporation, a powder of the same colour is formed, but it could not be purified. J. B. T.

Dinitrotoluenes. By C. HAEUSSERMANN and F. GRELL (*Ber.*, **27**, 2209—2210).—The authors confirm Beilstein's statement (*Annalen*, **155**, 25), that the product of the nitration of metanitrotoluene consists chiefly of dinitrotoluene [Me : NO$_2$: NO$_2$ = 1 : 3 : 4], melting at 61°. A small quantity of 1 : 3 : 5-dinitrotoluene, which melts at 92°, is also formed, a mixture of these isomerides remaining liquid for a considerable period. M. O. F.

Metanitrobenzylic Alcohol. By W. STAEDEL (*Ber.*, **27**, 2112). —This was prepared by P. Becker's method (*Ber.*, **15**, 2090) from very pure metanitrobenzaldehyde. It solidifies in a freezing mixture, and is capable of forming very large crystals. It melts at 27°. C. F. B.

Derivatives of Paracyanotoluene. By G. BANSE (*Ber.*, **27**, 2161—2171).—*Nitrotoluonitrile* [CN : NO$_2$: Me = 1 : 3 : 4], obtained by the action of fuming nitric acid on paratoluonitrile, forms yellowish-white needles, which melt at 107°. ω-*Chloronitrotoluonitrile* [CN : NO$_2$: CH$_2$Cl = 1 : 3 : 4] is prepared in the same way from paracyanobenzylic chloride; it crystallises in colourless prisms, which melt at 84°. When reduced with tin and hydrochloric acid, this compound yields *amidotoluonitrile* [CN : NH$_2$: Me = 1 : 3 : 4], melting at 81—82°. ω-*Chloronitrotoluic acid* [COOH : NO$_2$: CH$_2$Cl = 1 : 3 : 4] is obtained from the nitrile by the action of fuming hydrochloric acid at 100°; it melts at 140—141°, and forms a *silver* salt, which decomposes at 157°. The *amide* melts at 125°. The acid just

described reacts with aniline, forming *ω-anilidonitrotoluic acid* [COOH : NO₂ : CH₂·NHPh = 1 : 3 : 4], a basic substance, which melts and decomposes at 160°; the *hydrochloride* melts at 209°. With phenylhydrazine, the chloronitrotoluonitrile mentioned above forms *ω-phenylhydrazidonitrotoluonitrile*, which melts at 207°, whilst with potassium phthalimide the corresponding *phthalimido*-derivative is formed, melting at 194°. From this substance, on hydrolysis, and elimination of the phthalyl group, *nitrobenzylaminecarboxylic acid* [COOH : NO₂ : CH₂·NH₂ = 1 : 3 : 4], is obtained; it crystallises in nacreous plates, which melt at 243°; the *hydrochloride* melts at 249—250. *Cyanonitrobenzylic acetate* [CN : NO₂ : CH₂·OAc = 1 : 3 : 4], melting at 133°, is formed by heating an alcoholic solution of chloronitrotoluonitrile with sodium acetate; when hydrolysed, it yields *cyanonitrobenzylic alcohol*, crystallising in yellowish-white needles, which melt at 139°. On reducing the acetate with tin and hydrochloric acid, *cyanamidobenzylic alcohol* is formed; this melts at 102—103°.

Paracyanobenzylic alcohol, which melts at 133—134°, is formed by the action of potassium carbonate on paracyanobenzylic chloride; the *benzoate* melts at 123°. The *acetate* forms colourless leaves, which melt at 71—72° and yield parahydroxymethylbenzoic acid when hydrolysed; the nitration of the latter gives rise to a *dinitro*-derivative, which melts at 119—120°.

When paracyanobenzylic alcohol is nitrated, *cyanonitrobenzylic alcohol* [CN : NO₂ : CH₂OH = 1 : 2 : 4] is obtained, melting at 138°; it differs from the isomeride just described in its behaviour under the influence of acids and alkalis, this treatment causing the displacement of the nitro-group by hydroxyl, with subsequent hydrolysis of the resulting nitrile. *Cyanohydroxybenzylic alcohol*

[CN : OH : CH₂OH = 1 : 2 : 4],
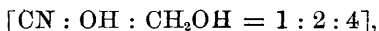
the intermediate product in this reaction, melts at 169°.

Paracyanobenzylic bromide is obtained by heating a mixture of paratoluonitrile and bromine in molecular proportion; it forms rhombic prisms, which melt at 115—116°. The *metanitro*-derivative melts at 106—107°. M. O. F.

Synthesis of Symmetrical Carvacrol. By E. KNOEVENAGEL (*Ber.*, **27**, 2347; compare Abstr., 1893, i, 697).—Metacamphor (Abstr., 1893, i, 419) when submitted to the action of bromine in acetic acid solution, yields an unstable dibromide; this readily loses the elements of hydrogen bromide, yielding symmetrical *carvacrol*, which melts at 54° and boils at 241°. It has the constitution [OH : Me : Prᵝ = 1 : 3 : 5]; its odour is reminiscent of phenol, and it dissolves in alkalis with great readiness, but no coloration is developed with ferric chloride. M. O. F.

Creosotes from Beech. Tar and Oak Tar. By A. BÉHAL and E. CHOAY (*Compt. rend.*, **119**, 166—169; compare this vol., i, 508).— Beech-tar creosote, boiling between 200° and 220°, contains in 100 parts, monophenols 39, guaiacol 19·72, creosol and its homologues

39·98. When fractionated, 367 parts, boiling at 210—220° (sp. gr. at 15° = 1·085), are obtained for every 1,000 parts boiling at 200—210°; sp. gr. at 17° = 1·085. The latter contains, in 100 parts, monophenols 39, guaiacol 26·48, creosol and its homologues 32·14.

Oak-tar creosote, boiling at 200—210°, sp. gr. 1·068, contains, in 100 parts, monophenols 55, guaiacol 14, creosol and its homologues 31.

The monophenols consist approximately of ordinary phenol 13, orthocresol 26, meta- and para-cresol 29, orthethylphenol 9, metaxylenol [1 : 3 : 4] 5, metaxylenol [1 : 3 : 5] 2·5, other phenols 15·5 = 100·00.

Combining these figures with those previously given, it would seem that beech-tar creosote contains phenol 5·20, orthocresol 10·40, meta- and para-cresol 11·60, orthethylphenyl 3·06, metaxylenol [1 : 3 : 4] 2·00, metaxylenol [1 : 3 : 5] 1·00, various phenols 6·20, guaiacol 25·00, creosol and its homologues 35·00 = 100. These results are far from being in agreement with the accepted view that creosote consists chiefly of guaiacol.   C. H. B.

Derivatives of 1 : 3-Diketocyclohexane (Dihydroresorcinol). By E. KNOEVENAGEL (*Ber.*, **27**, 2337—2345; compare Vorländer, this vol., i, 528).—The author studying the action of ethylic malonate on ethylic benzylideneacetoacetate in the presence of diethylamine, has arrived at substantially identical results with those described by Vorländer (*loc. cit.*), the product of the reaction being a crystalline *compound* which melts at 148°, and has the constitution

$$COMe \cdot CH(COOEt) \cdot CHPh \cdot CH(COOEt)_2.$$
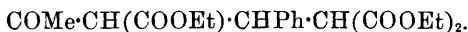
By the use of alcoholic potash in the place of diethylamine, *diethylic 5-phenyl-1 : 3-diketocyclohexane-4 : 6-dicarboxylate* is obtained in the form of its potassium salt; it melts at 156°. Hydrolysis of this substance leads to the formation of 5-phenyl-1 : 3-diketocyclohexane melting at 187—188° (compare Vorländer, *loc. cit.*; also Michael and Freer, Abstr., 1891, 914). By the action of phosphorus pentachloride (2 mols.) on the latter compound, an oil is formed, probably having the constitution $CHPh \big\langle {CH:CCl \atop CH:CCl} \big\rangle CH_2$; it is a highly refractive liquid boiling at 178—179° (22 mm.). Treatment with aniline gives rise to a *substance* which crystallises in lustrous scales, and decomposes without fusion. The product from ethylic benzylideneacetoacetate and ethylic malonate, under the influence of alcoholic hydrochloric acid, yields a *compound* which melts at 85°, and closely resembles β-phenyl-γ-acetylbutyric acid (Vorländer, *loc. cit.*); it differs from it, however, as regards solubility, and it will be the subject of future investigation.

In the above-mentioned reaction, ethylic ethylmalonate may be substituted for ethylic malonate; the *compound* formed melts at 154°. The product of the action of alcoholic hydrochloric acid on it melts at 90°. By acting on ethylic phenyldihydroresorcylate (Vorländer, *loc. cit.*) with phenylhydrazine, a *substance* of the formula $C_{20}H_{22}N_2O_3$ is obtained; it forms yellow scales, and melts at 130°.

Diethylic 5-*methyl*-1 : 3-*diketocyclohexane*-4 : 6-*dicarboxylate,*

$$CHMe<^{CH(COOEt) \cdot CO}_{CH(COOEt) \cdot CO}>CH_2,$$
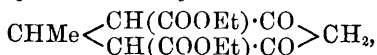
is obtained by the interaction of ethylic malonate with ethylic ethylideneacetoacetate, in molecular proportion, in the presence of caustic potash; it melts at 85°, and, when crystallised from water, retains $1H_2O$, this form melting at 75°. When this substance is heated with phenylhydrazine (2 mols.), *hexamethylenedipyrazolone*, of the constitution

$$\begin{matrix} NPh \cdot N : C- CH_2 -C : N \cdot NPh \\ CO \underline{\qquad} CH \cdot CHMe \cdot CH \cdot CO \end{matrix}, \text{ is formed; it melts at 315°, and is}$$

insoluble in all indifferent solvents. Acids and alkalis dissolve it, however, the *sulphate* forming small, white needles; the *sodium* and *potassium* salts are hygroscopic.　　　　　　　　　　M. O. F.

New Synthesis of Phenol-alcohols. By L. LEDERER (*J. pr. Chem.*, [2], **50**, 223—226).—Phenol-alcohols can be prepared, on the large scale also, by condensation of formaldehyde with phenols. The alcohol-group takes by preference the ortho- and para-positions, and it is possible, by varying the condensation agent, to obtain either an almost pure ortho-product, or a mixture of this with the para-isomeride. Below are given the melting points of various crystallised phenol-alcohols that have been obtained by this method; they give blue or green colours with ferric chloride, mixed sometimes with a shade of red.

Hydroxybenzylic alcohols. Ortho (*saligenin*), 86°, sublimes readily. *Para,* 110°. 1 : 2-*Hydroxymethylbenzylic alcohol,* 40°. 1 : 3-*Hydroxymethylbenzylic alcohol,* 107°. 1 : 4-*Hydroxymethylbenzylic alcohols;* (*a*) 107°, (*b*) 133°. 1 : 5 : 2-*Hydroxymethylpropylbenzylic alcohol,* 86°. 1 : 2 : 4-*Hydroxymethoxyallylbenzylic alcohol,* 37°.　　　　C. F. B.

Synthesis of Phenol-alcohols. By O. MANASSE (*Ber.*, **27**, 2409—2413).—In this preliminary communication, the author states that he, like Lederer (preceding abstract), has obtained alcohols from phenols by condensing them with formaldehyde. The action takes place at the ordinary temperature when caustic soda is used as the condensing agent; potash, sodium carbonate, potassium carbonate, lime, zinc oxide, lead oxide, zinc dust, sodium acetate, or potassium cyanide may also be used.

From phenol was obtained a mixture of para- (m. p. 111—112°) and ortho- (m. p. 82°) hydroxybenzylic alcohols. From guaiacol, vanillic alcohol (m. p. 115°), or an unstable compound (m. p. 110—111°) of this with formaldehyde (1 mol.). From paracresol, homosaligenin (m. p. 105°) [OH : Me : CH_2OH = 1 : 4 : 2]; from metacresol, a 1 : 4 : 3-isomeride (m. p. 117—118°), together with another of unknown constitution (m. p. 105°). From thymol, probably parathymotic alcohol (m. p. 120—121°) (Kobek, Abstr., 1884, 56). From orthohydroxyquinoline, an alcohol, $HO \cdot C_9NH_5 \cdot CH_2 \cdot OH$, which forms a compound (m. p. 141—142°) with 1 mol. of formaldehyde. β Naphthol yields no alcohol, but paradihydroxynaphthylmethane.　　　　　　　　　　　　　　　　　C. F. B.

Eugenol and Isoeugenol. By A. EINHORN and C. FREY (*Ber.*, **27**, 2455—2460).—Eugenol, $OH \cdot C_6H_3(OMe) \cdot CH_2 \cdot CH:CH_2$, is converted into isoeugenol, $OH \cdot C_6H_3(OMe) \cdot CH:CH \cdot CH_3$, when it is heated quickly to 220° with 4 parts of caustic potash. When phosphorus oxychloride is added to a cooled solution of eugenol or isoeugenol, in aqueous soda, the *phosphates*, $PO[O \cdot C_6H_3(OMe) \cdot C_3H_5]_3$, are formed; in both cases they were obtained as oils. When 2 : 4 : 1-dinitrochlorobenzene and eugenol are dissolved in absolute alcohol, and potash is added to the solution, a yellow *dinitrophenylic eugenol ether*, $C_6H_3(NO_3)_2 \cdot O \cdot C_6H_3(OMe) \cdot C_3H_5$, melting at 114—115°, is formed; the yellow isomeride obtained from isoeugenol melts at 129—130°, and when oxidised, yields white *vanillin dinitrophenylic ether*, $C_6H_3(NO_2)_2 \cdot O \cdot C_6H_3(OMe) \cdot CHO$, which melts at 131°, and can also be prepared by the action of dinitrochlorobenzene on vanillin. Picrylchloride and eugenol, when treated with caustic potash in alcoholic solution, yield yellow *picryleugenol*, $C_6H_2(NO_3)_3 \cdot O \cdot C_6H_3(OMe) \cdot C_3H_5$, melting at 92—93°; isoeugenol yields a yellow isomeride which melts at 145—146°, and, when oxidised with chromic acid in acetic acid solution, yield *picrylvanillin*, $C_6H_2(NO_3)_3 \cdot O \cdot C_6H_3(OMe) \cdot CHO$, together with yellow *picrylvanillic acid*. The former melts at 114—116°, and can also be prepared from picryl chloride and vanillin; the latter melts at 184—186°, and is decomposed by potash into picric and vanillic acids. Picrylvanillin is also readily decomposed; with phenylhydrazine, it yields picrylphenylhydrazine (the yellow *acetyl-derivative* of which melts at 236°), and with aniline picrylanilide and vanillin.

<div align="right">C. F. B.</div>

Phenacyleugenols and Acetonyleugenols. By A. EINHORN and C. v. HOFE (*Ber.*, **27**, 2461—2466).—Eugenol and isoeugenol condense with bromacetophenone, or chloracetone, when the two substances are mixed in alcoholic solution, and alcoholic potash is added; *phenacyl-derivatives*, $CPhO \cdot CH_2 \cdot O \cdot C_6H_3(OMe) \cdot C_3H_5$, or *acetonyl-derivatives*, $CMeO \cdot CH_2 \cdot O \cdot C_6H_3(OMe) \cdot C_3H_5$, being formed. The isoeugenol-derivatives, when treated with potassium permanganate, are oxidised to the corresponding vanillin or vanillic acid derivatives, the $-C_3H_5 (= -CH:CH \cdot CH_3)$ group being converted into -CHO or -COOH respectively.

Phenacyleugenol (eugenolacetophenone) melts at 47·5°, and forms a yellowish *phenylhydrazone*, melting at 82°, and an *oxime* melting at 81—82°. *Phenacylisoeugenol (isoeugenolacetophenone)* melts at 83°, and yields a yellow *phenylhydrazone* melting at 115·5°, and an *oxime* melting at 141—142°; boiling with alcoholic hydrochloric acid converts it into *di-isoeugenolacetophenone*, $C_{36}H_{36}O_6$, melting at 119—120°. When oxidised, it yields yellow *phenacylvanillic (acetophenonevanillic) acid* melting at 169°, and *phenacylvanillin (acetophenonevanillin)*, which melts at 128°, and forms a *monophenylhydrazone*,

$$CPhO \cdot CH_2 \cdot O \cdot C_6H_3(OMe) \cdot CH:N_2HPh,$$
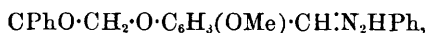
melting at 161°, but no diphenylhydrazone; the vanillin derivative and its phenylhydrazone can also be prepared by the action of bromacetophenone on vanillin and its phenylhydrazone respectively.

Acetonyleugenol is an oil, and its *phenylhydrazone* melts at 93°. *Acetonylisoeugenol* is also an oil; its *phenylhydrazone* melts at 145°.

C. F. B.

Conversion of Eugenol into Isoeugenol. By F. TIEMANN (*Ber.*, **27**, 2580—2581).—This molecular rearrangement is dependent on the temperature to which the liquid is exposed, and not on the nature of the solvent employed. The conditions most favourable to the conversion of eugenol into isoeugenol have been already described by the author (Abstr., 1892, 45).

M. O. F.

α-Phenylethylamine. By M. KANN and J. TAFEL (*Ber.*, **27**, 2306—2309).—α-Phenylethylamine, $NH_2 \cdot CHMePh$, has already been prepared by the authors by reducing the hydrazone of acetophenone. It is very easily obtained by reducing either the oxime or hydrazone of acetophenone with sodium in boiling alcohol. The *nitrite*, obtained by shaking the hydrochloride with silver nitrite, melts at 75° with evolution of gas. The *acetyl compound* boils at 292—293° under 752 mm. pressure, and melts at 57°. The *benzoyl compound* crystallises in white needles, and melts at 120°.

Benzylidene-α-phenylethylamine, obtained by the action of benzaldehyde on phenylethylamine, is a colourless oil. It decomposes when distilled under ordinary pressure, boils at 273—275° under 14 mm. pressure, does not solidify at −15°, and is decomposed into its constituents when boiled with dilute acids.

α-Phenylethylcarbamide, obtained by the action of potassium cyanate on phenylethylamine hydrochloride, melts at 137°, and decomposes about 210°.

Di-α-phenylethyloxamide, obtained by warming α-phenylethylamine with ethylic oxalate on the water bath, sinters at 180°, and melts at 185°.

E. C. R.

γ-Phenylpropylamine and its Conversion into Allylbenzene. By L. SENFTER and J. TAFEL (*Ber.*, **27**, 2309—2313).—*Benzoyl-γ-phenylpropylamine*, obtained by the Schotten-Baumann method, forms crystalline crusts, and melts at 57—58°. *γ-Phenylpropylcarbamide*, obtained from the base in the usual way, crystallises in lustrous leaflets, melts at 143°, and decomposes, when heated above 200°, with evolution of ammonia. *γ-Phenylpropylphenylthiocarbamide*, obtained from the base and phenylthiocarbimide, crystallises in colourless needles, and melts at 103°.

γ-Phenylpropylamine, $CH_2Ph \cdot CH_2 \cdot CH_2 \cdot NH_2$, combines energetically with carbon bisulphide to yield a white, crystalline mass which melts at 90°, and, on analysis, gave numbers corresponding with the formula of phenylpropylamine phenylpropyldithiocarbamic acid, $C_{19}H_{26}N_2S_2$.

Dimethyl-γ-phenylpropylamine, $CH_2Ph \cdot CH_2 \cdot CH_2 \cdot NMe_2$, is a colourless liquid, boils at 225° under 754 mm. pressure, has a faint odour, and reacts strongly alkaline in aqueous solutions. The *platinochloride* melts at 149°. The *picrate* crystallises in thin needles, and melts at 99°.

Trimethyl-γ-phenylpropylammonium iodide is obtained by boiling

2 s 2

phenylpropylamine with excess of methylic iodide and methylic alcohol in a reflux apparatus, and treating the product with excess of 10 per cent. sodium hydroxide. It melts at 175·5°.

Allylbenzene, $CH\cdot Ph{:}CHMe$, is obtained by heating the preceding compound with excess of silver oxide, and, after distilling the product, treating it with dilute sulphuric acid and extracting with ether. It is a colourless liquid, boils at 174—176°, does not solidify at − 16°, and has an odour resembling that of petroleum. The *dibromide* melts at 65—66°. When the sulphuric acid solution, obtained in the preparation of this compound is treated with solid potash, it yields dimethyl-γ-phenylpropylamine. E. C. R.

Action of Phosphorus Tri- and Penta-chlorides on Ortho-toluylenediamine. By O. HINSBERG (*Ber.*, **27**, 2178—2180).—A *compound*, which probably has the constitution

$$C_6H_3Me{<}^{NH}_{NH}{>}PO\cdot NH\cdot C_6H_3Me\cdot NH_2,$$
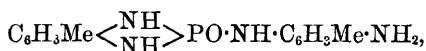
is obtained by the action of either of the phosphorus chlorides on ortho-toluylenediamine, the action in the case of phosphorus trichloride being accompanied by the liberation of hydrogen phosphide and amorphous phosphorus. It forms delicate, colourless needles, which melt at about 200°. Hydrolysis is effected by dilute acids or alkalis, phosphoric acid being eliminated with regeneration of the base. In the alcoholic solution, ferric chloride develops a green coloration, which becomes reddish-violet, finally changing to red when warmed. M. O. F.

Stereoisomerism of the Diazo-compounds; Constitution of Isodiazo-compounds. By E. BAMBERGER (*Ber.*, **27**, 2582—2595).— An attack is made on the system by which Hantzsch explains the existence of compounds isomeric with azo-derivatives (this vol., i, 452). The criticism is too detailed to be dealt with in an abstract, the author's main points, however, being the accord in which the nitros-amine formula stands with recorded facts, and the insufficiency of the evidence adduced by Hantzsch in support of his hypothesis.

M. O. F.

The " Stereoisomeric " Diazoamido-compounds of Hantzsch. By E. BAMBERGER (*Ber.*, **27**, 2596—2601; compare Hantzsch, this vol., i, 549).—The existence of these substances is obviously of paramount importance to the controversy referred to in the preceding abstract. Careful examination of the so-called benzene-syndiazoanilide and paratoluenesyndiazotoluidide (*loc. cit.*), establishes their identity with bisdiazobenzeneanilide and bisparadiazotoluene-paratoluidide (Pechmann and Frobenius, this vol, i, 283) respectively. The two compounds are converted into diazoamidobenzene and diazoamidotoluene under the influence of alcoholic ammonia ; this fact coincides with the observation of Hantzsch, the change having been regarded by this investigator, however, as a transforma-tion of the syn- into the anti-modification. M. O. F.

Constitution of Benzenediazoic Acid. By E. BAMBERGER (*Ber.*, **27**, 2601—2611).—The evidence in support of the author's nitramine formula for this substance is recapitulated and followed by a criticism of the constitution advocated by Hantzsch (this vol., i, 456). M. O. F.

Diazoamidobenzene. By W. BECKH and J. TAFEL (*Ber.*, **27**, 2315—2316).—*Sodium diazoamidobenzene*, NNaPh·N:NPh, is obtained by dissolving sodium in an ethereal solution of diazoamidobenzene; on evaporation of the ether, it is deposited in long, reddish-yellow needles, which are unstable in moist air, being resolved into diazoamidobenzene and sodium hydroxide. Iodine removes sodium from the compound, whilst the action of benzoic chloride gives rise to *benzoyldiazoamidobenzene*, forming yellowish-brown needles, which melt and decompose at 131°. When boiled with alcohol, evolution of gas takes place, and the odour of aldehyde becomes perceptible; in this property it resembles acetyldiazoamidobenzene. If an ethereal solution of hydrogen chloride is added to benzoyldiazoamidobenzene dissolved in benzene, diazobenzene chloride is formed and may be separated by agitating with water, benzanilide remaining undissolved. M. O. F.

Paradinitrodiazoamidobenzene: A Correction. By R. MELDOLA and F. W. STREATFEILD (*Ber.*, **27**, 2201—2202).—The authors amend a statement of Pawlewski (*Ber.*, **27**, 1565) to the effect that paraphenylenediamine is the sole product obtained by them on reducing the azo-compound in question. This is not the case, products resulting from reduction with sulphide of ammonium in alkaline solution having been already described by the authors (Trans., 1886, 628). They attributed the magenta coloration observed on dissolving the azo-compound in alcoholic potash to the formation of an alkali salt, and do not regard it as indicating an initial stage of the reduction. In connection with this point, analogous salts have been described, and it is found that they are all coloured substances, the silver and cadmium salts especially exhibiting a brilliant red tint.
M. O. F.

Phenylhydrazine. By BERTHELOT (*Compt. rend.*, **119**, 5—12).— Phenylhydrazine when exposed to air quickly becomes yellow; the change is more distinct if it is previously dissolved in water or dilute acids, brown insoluble matter separating from the solution. This change is due to oxidation, and is most marked when the solution of phenylhydrazine hydrochloride is mixed with sodium acetate; oxygen is absorbed and an equal volume of nitrogen is liberated, this ratio being maintained at every stage of the action, which is complete in 12 hours at 100°. Oily uncrystallisable diphenylhydrazine separates from the liquid.

Pure anhydrous phenylhydrazine when heated at 100° with oxygen in closed vessels absorbs 1·1 to 1·25 atoms of oxygen, and 1·6—1·7 atoms of nitrogen is liberated. The products are resinous, uncrystallisable, and insoluble in water.

Pure liquid phenylhydrazine absorbs moisture from the air, and after a few hours crystallises if the surrounding temperature is below 22°. The hydrate can also be obtained by mixing the compound with rather less than half its volume of water, and allowing the mixture to evaporate spontaneously ; beautiful colourless crystals separate, which soon become yellow, and eventually orange, in consequence of slow oxidation. The most rapid method of preparing the hydrate is to mix 10 c.c. of phenylhydrazine with 0·9 c.c. of water. It has the composition $2C_6H_8N_2 + H_2O$, and melts at 24·1°, whilst anhydrous phenylhydrazine melts at 17·5°, and not at 23° as is commonly stated.

Calorimetric experiments give the following results.

Molecular heat of fusion of phenylhydrazine . . . .   −2·645 Cals.
Heat of formation of the hydrate from liquid constituents . . . .   +8·41   ,,
Heat of formation of the hydrate from liquid water and solid phenylhydrazine . . . .   +3·12   ,,
Heat of formation of the hydrate from solid constituents . . . .   +1·55   ,,
Heat of fusion of the hydrate . . . .   +8·04   ,,

The direct combination of liquid phenylhydrazine and water yields a liquid hydrate with development of heat = 0·37 Cal. If a fragment of crystallised hydrate is added, crystallisation commences immediately and proceeds slowly, even after the mass has apparently become solid. It is, therefore, practically impossible to determine the heat of formation of the solid hydrate by direct synthesis.

The heats of neutralisation are as follows.

	Liquid phenylhydrazine.		Dissolved phenylhydrazine.	
	1st equivt.	2nd equivt.	1st equivt.	2nd equivt.
Hydrochloric acid	+ 8·70 Cal.	—	+ 8·19 Cal.	—
Sulphuric acid	+ 9·11 ,,	+ 10·28 Cal.	+ 8·82 ,,	+ 9·99 Cal.
Acetic acid	+ 5·42 ,,	—	+ 5·13 ,,	—

In the case of the sulphate, the first equivalent of the base develops less heat than the second ; in the case of the acetate, the addition of a second equivalent of acid causes a further development = 1·26 Cals., probably because the normal acetate dissociates in contact with water. An excess of phenylhydrazine causes a distinct increase in the heat developed on formation of the normal salts.

Phenylhydrazine does not react with carbonic oxide, and does not absorb carbonic anhydride from the air. Moreover the hydrochloride liberates only a small quantity of gas from solutions of normal sodium carbonate, and that very slowly ; if, on the other hand, the hydrochloride is added to a solution of sodium hydrogen carbonate there is rapid evolution of gas, with development of heat = 3·1 Cal. for the complete reaction in presence of sufficient water to dissolve the whole

of the carbonic anhydride. For a complete reaction, as in the case of ammonium salts,

$$2C_6H_8N_2 \text{ diss.} + CO_2 \text{ diss. develops } +4\cdot8 \text{ Cals.}$$
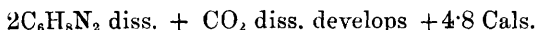
The difference between the heats of formation of the sulphate and chloride $+1\cdot21$ Cal. is of the same order of magnitude as in the case of the stable alkali salts, but the difference between acetate and chloride is much greater, doubtless in consequence of the dissociation of the former, and the difference is still greater in the case of the carbonates. When a solution of phenylhydrazine sulphate or hydrochloride is mixed with sodium acetate, there is distinct absorption of heat, and with sodium carbonate this absorption is still greater.

These results afford further confirmation of the author's law, that in the case of mixtures of dissolved salts the strong acid unites with the strong base with almost complete formation of that salt which is most stable in presence of water and is also the salt with the highest heat of formation in the solid state.　　　　C. H. B.

Solubility of Phenylhydrazine in Aqueous Solutions of Salts of the Alkalis. By R. OTTO (*Ber.*, **27**, 2131—2133).—The author finds that phenylhydrazine dissolves readily in aqueous solutions of salts of the sulphinic acids, sulphonic acids, higher fatty acids, gallic acids, and of salicylic acid. The phenylhydrazine is only extracted with difficulty from the solutions by means of ether.　　H. G. C.

Action of Phosphorus Pentachloride on Symmetrical Benzoylphenylhydrazine. By H. v. PECHMANN and L. SEEBERGER (*Ber.*, **27**, 2121—2125).—The action of phosphorus pentachloride on symmetrical benzoylphenylhydrazine gives rise to a number of byeproducts in addition to the imidochloride already described (this vol., i, 240); these consist chiefly of benzoylhydrazides of phosphoric acid. The first product of the action is probably the *amidochloride*, $CPhCl:N\cdot NPh\cdot POCl_2$, which has not, however, been isolated. It is a syrup, which is decomposed by water with re-formation of benzoylphenylhydrazine, but if left for a time, or on treatment with alcohol, it yields at least six different compounds.

When the ethereal solution is treated with methylic alcohol, or better with phenol, it is converted into the imidochloride, $CPhCl:N:NHPh$, already described, which remains for the most part undissolved, whilst the solution contains the *lactone* of *symmetrical benzoylphenylhydrazidophosphoric acid*, $CPh\begin{subarray}{l} N\cdot NPh \\ \diagdown O\cdot PO\cdot OH \end{subarray}$; this forms silky, matted needles or lustrous prisms, melts at 161°, and is resolved by boiling acids or alkalis into phosphoric acid and symmetrical benzoylphenylhydrazine. It dissolves in cold alkalis, but loses this property after treatment with potash and methylic iodide; the resulting neutral compound yields phenylhydrazine on hydrolysis, proving that the source of the acid hydrogen atom of the original compound is the phosphoric acid group.

Symmetrical disbenzoylphenylhydrazidophosphoric acid,

$$(NHBz \cdot NPh)_2 POOH,$$

is obtained from the mother liquors of the foregoing compound, and may also be obtained in large quantity from the syrupy amidochloride by pouring it into an excess of methylic alcohol. It forms lustrous prisms or matted needles, melts at 131—132°, is soluble in alkalis, and reduces mercuric oxide in the cold. The *lactone* of this acid separates from the ethereal solution of the product of the action of phosphorus pentachloride and benzoylphenylhydrazine. If left for some days, it crystallises in small prisms melting at 164·5°. It is insoluble in alkalis, and does not reduce mercuric oxide. Another compound which appears to have the same composition is prepared by heating the benzoylphenylhydrazine with the pentachloride for several hours, and, after crystallising from a mixture of chloroform and alcohol, melts at 220°; it also is insoluble in alkalis, and does not reduce mercuric oxide.   H. G. C.

Hydrazidoacetaldehyde II. By E. FISCHER and P. HUNSALZ (*Ber.*, **27**, 2203—2208; compare this vol., i, 169).—The authors prefer to express the constitution of acetalylphenylthiosemicarbazide by the formula $NHPh \cdot CS \cdot N(NH_2) \cdot CH_2 \cdot CH(OEt)_2$, rather than by that already indicated (*loc. cit.*). They are led to this conclusion by the formation of acetalylphenylthiocarbamide under the influence of nitrous acid, and also by the fact that on elimination of two molecular proportions of alcohol, acetalylphenylthiosemicarbazide is converted

into *phenylthioamidodihydroimidazole*, $CS {<}^{N(NH_2) \cdot CH}_{NPh \underline{\qquad} CH}$, the reaction

being effected by heating in a closed tube with hydrochloric acid. The substance melts at 89°. It is indifferent towards Fehling's solution, and blackens mercuric oxide. The *hydrochloride* melts at 165°; the *benzylidene*-compound forms shining yellow plates, which melt at 140—141°. Treatment with nitrous acid gives rise to phenylimidazole.

Acetalylphenylsemicarbazide, $NHPh \cdot CO \cdot N_2H_2 \cdot CH_2 \cdot CH(OEt)_2$, is prepared by warming hydrazidoacetal with phenylcarbimide; it crystallises in colourless needles, which melt at 65—66°. If excess of phenylcarbimide is used, the *compound*

$$N_2H(CO \cdot NHPh)_2 \cdot CH_2 \cdot CH(OEt)_2$$
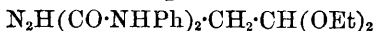
is formed, melting at 171—172°.

Acetalyldimethylhydrazonium iodide, $NH_2 \cdot NMe_2I \cdot CH_2 \cdot CH(OEt)_2$, is formed by the prolonged action of methylic iodide on hydrazidoacetal; it is converted into the *chloride* by agitation with silver chloride. The *platinochloride* separates from hot water in large, reddish-yellow plates which melt at 165°. A *substance* having reducing properties, and consisting most probably of the aldehyde $COH \cdot CH_2 \cdot NMe_2Cl \cdot NH_2$, is formed from the chloride by the action of strong hydrochloric acid; its *platinochloride* is a bright yellow, amorphous powder.

M. O. F.

Phenylhydrazone of Salicylaldehyde. By H. BILTZ (*Ber.*, **27**, 2288—2290).—An *isosalicylaldehyde phenylhydrazone* is obtained from

the mother liquors of the ordinary modification when salicylaldehyde, dissolved in light petroleum, is treated with an ethereal solution of phenylhydrazine. It melts at 104—105°, crystallises in triclinic needles, dissolves in sodium hydroxide, and is precipitated unchanged by acids; when warmed with alcohol it is converted into the ordinary modification melting at 142°.

A *polymeric salicylaldehydephenylhydrazone*, $(C_{13}H_{12}N_2O)_2$, is obtained when the hydrazone is heated with a 2 per cent. solution of potassium hydroxide in 50 per cent. alcohol. It crystallises from nitrobenzene in monoclinic crystals, and melts at 265°.   E. C. R.

Benzhydroximic Chloride. By A. WERNER and H. BUSS (*Ber.*, **27**, 2193—2201).—This compound was prepared with the object of converting it into phenylnitrolic acid by treatment with silver nitrite; the reaction, however, proceeds in a different direction, nitrous acid being eliminated with formation of benziledioxime peroxide.

Benzhydroximic chloride, $OH \cdot N{:}CPhCl$, is obtained by passing a current of dry chlorine gas into a well-cooled mixture of anti- or syn-benzaldoxime and chloroform, until the evolution of hydrogen chloride is accompanied by a change in the colour of the liquid from green to yellow. On allowing the chloroform to evaporate, benzhydroximic chloride is deposited in compact prisms which melt at 48°. Under other conditions, the action of chlorine on the synaldoxime leads to the formation of the antialdoxime hydrochloride, the final product consisting of benziledioxime peroxide.

Benzhydroximic chloride is stable towards water. Treatment with sodium carbonate removes hydrogen chloride, with formation of benziledioxime peroxide, whilst decomposition by sodium ethoxide gives rise to the formation of ethylbenzhydroximic acid and diphenylcarbamide. Towards bases, it displays great activity, ammonia producing benzenylamidoxime; the *dipropyl*-derivative of this, melting at 62—66°, is obtained by adding dipropylamine (2 mols.) to an ethereal solution of benzhydroximic chloride.

Dibenzhydroximic acid, $OH \cdot N{:}CPh \cdot OBz$, which melts at 95°, is prepared by the action of silver benzoate on benzhydroximic chloride; it, however, spontaneously undergoes molecular rearrangement, the isomeric dibenzhydroxamic acid, $OH \cdot CPh{:}N \cdot O \cdot COPh$ (benzoyl benzhydroxamate), being formed.

It has already been mentioned that the peroxide of benzildioxime is obtained by the action of sodium carbonate on benzhydroximic chloride, hydrogen chloride being eliminated; an oily substance which rapidly solidifies, is first formed, and this is regarded by the authors as the intermediate product of the action, yielding benziledioxime peroxide by polymerisation. To this substance the authors assign the constitution $Ph \cdot C{:}NO$, a view which is strengthened by the formation of hydroxylamine on hydrolysis. The action of caustic potash on benzhydroximic chloride proceeds in two directions, either like that of sodium carbonate, or, with the displacement of chlorine by hydroxyl.

These observations lead the authors to conclude that the substance

obtained by the action of sodium carbonate on the oxime of hydroxy-isonitrosoacetone nitrite (Behrend and Schmitz, Abstr., 1893, i, 304),

has the constitution
$$\begin{array}{l} \text{O·N:C·CMe:N·OH} \\ \text{O·N:C·CMe:N·OH·} \end{array}$$
M. O. F.

Organometallic Compounds. By G. Périer (*Compt. rend.*, **119**, 90—92).—When acetanilide (2 mols.) and freshly-prepared anhydrous aluminium chloride (1 mol.) are gently heated together, a violent action takes place, with formation of a homogeneous liquid, which afterwards solidifies to a translucent, yellow mass, but there is no sensible evolution of hydrogen chloride. The same reaction takes place in presence of carbon bisulphide. The product, $(C_8H_9ON)_2Al_2Cl_6$, is insoluble in all solvents which do not decompose it. With water, it yields aluminium chloride and acetanilide. Absolute alcohol dissolves it without any precipitation of aluminium hydroxide, but, on evaporation, acetanilide separates in crystals. Butyranilide forms a similar compound, $(C_{10}H_{13}ON)_2,Al_2Cl_6$.

Acetoparatoluidine and its substitution derivatives also yield analogous products, which decompose in contact with water or when exposed to air.

Anhydrous ferric chloride likewise combines with amides and amines, but the compounds, which probably have the composition $R_2Fe_2Cl_6$, are difficult to purify. C. H. B.

Aromatic Chlorophosphines. By A. Michaelis (*Ber.*, **27**, 2556 —2559).—The author has previously suggested the term chlorophosphine for the group PCl_2; he now proposes that compounds in which this radicle is linked to oxygen shall be termed "*o*-chlorophosphines," corresponding derivatives of phosphorus oxychloride being called "*o*-oxychlorophosphines," and the acid derivatives of each "*o*-phosphinous acid" and "*o*-phosphinic acid" respectively. Thus $OPh·PCl_2$ is phenol-*o*-chlorophosphine, $(PhO)_3P$ is triphenol-*o*-phosphine, and $PhO·PO(OH)_2$ phenyl-*o*-phosphinic acid. Compounds containing chlorophosphine linked to nitrogen or sulphur are distinguished by the letters *n* or *s*, thus, $NHPh·POCl_2$ is aniline-*n*-oxychlorophosphine, and $NHPh·PO(OH)_2$ aniline-*n*-phosphinic acid. The paper concludes with an abstract of Kunz's, Knauer's, and Schulze's investigations of these classes of compounds (following abstracts). J. B. T.

Note.—This proposed use of *o*- is very misleading, as it is apt to be confounded with the *o*- used to signify ortho-.—[Editors.]

Phenol and Naphthol Chlorophosphines. By P. Kunz (*Ber.*, **27**, 2559—2565).—By the interaction of methoxybenzene or ethoxybenzene, phosphorus trichloride, and pure aluminium chloride, phenylchlorophosphine is formed, but, with commercial aluminium chloride, the methoxy- or ethoxy-phenylchlorophosphine, $OEt·C_6H_4·PCl_2$, is obtained.

α-Naphtholchlorophosphine, $C_{10}H_7·O·PCl_2$, is prepared from phosphorus trichloride and *α*-naphthol, and from *α*-ethoxynaphthalene, phosphorus trichloride, and aluminium chloride; it is a colourless

liquid, soluble in anhydrous alcohol and ether, and boils at 174—176° (15 mm.), the sp. gr. = 1·0776. *α-Naphtholphosinous acid*, $C_{10}H_7 \cdot O \cdot PO_2H_2$, prepared by the action of cold water on the preceding compound, is a colourless, crystalline powder, melting at 82°; like the chlorophosphine, it is resolved into phosphorous acid and α-naphthol by the prolonged action of water. The *phenylhydrazine salt*, $C_{10}H_7 \cdot O \cdot PO_2H \cdot NH_3 \cdot NHPh$, is a colourless powder, melting at 83°. *α-Naphtholoxychlorophosphine*, formed from α-naphthol and phosphorus oxychloride, is a thick, colourless liquid, boils at 325—327° or at 198—200° (20 mm.); the sp. gr. = 1·0889 at 15°. *Di-α-naphtholoxychlorophosphine* and normal α-naphthol phosphate are formed in small quantity with the preceding compound. *α-Naphtholphosphinic acid*, $C_{10}H_7 \cdot O \cdot PO(OH)_2$, prepared by the action of cold water on the chlorophosphine, is colourless and crystalline, melts at 142°, and is hydrolysed by warm water. The *phenylhydrazine salt*,

$$C_{10}H_7 \cdot O \cdot PO(OH)O \cdot NH_3 \cdot NHPh,$$
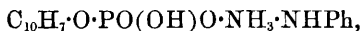
crystallises in thin plates, melting at 188°. The *diphenylhydrazine salt*, $C_{10}H_7 \cdot O \cdot PO(O \cdot NH_3 \cdot NHPh)_2$, is colourless, and melts at 147—148°. *Ethylic α-naphtholphosphinate*, $C_{10}H_7 \cdot O \cdot PO(OEt)_2$, is a colourless, viscid liquid, decomposing when distilled; its sp. gr. is 1·0441. *Ethylic di-α-naphtholphosphinate*, $(C_{10}H_7O)_2PO(OEt)_2$, is obtained from alcohol and di-α-naphtholoxychlorophosphine; it crystallises in plates and melts at 31—32°. The *phenylhydrazone*,

$$C_{10}H_7 \cdot O \cdot PO(NH \cdot NHPh)_2,$$
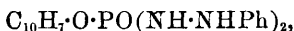
prepared from the chlorophosphine and phenylhydrazine, is crystalline, and melts at 168—169°.

β-Naphtholchlorophosphine is a colourless liquid, formed in a similar manner to the α-derivative; it boils at 179—181° (15 mm); its sp. gr. is 1·0781 at 15°. *β-Naphtholphosphinous acid* is colourless and crystalline, melts at 111°, and, like the chlorophosphine, readily becomes red. The *phenylhydrazine salt* melts at 98—99°. *β-Naphtholoxychlorophosphine*, from β-naphthol and phosphorus oxychloride, is colourless or slightly red, melts at 39°, and boils at 204—205° (20 mm.). *β-Naphtholphosphinic acid* is crystalline, and melts at 167°; it is hydrolysed by boiling with water, more rapidly by dilute acids, but is not attacked by alkalis. The *diphenylhydrazine* and the *hydrogen phenylhydrazine salts* are crystalline, and melt at 168° and 180° respectively. The *ethylic salt* is a viscid liquid; its sp. gr. is 1·0439. The *phenylhydrazone* crystallises from glacial acetic acid and melts at 198°. *Di-β-naphtholphosphinic acid*, $PO(O \cdot C_{10}H_7)_2 \cdot OH$, is formed together with the oxychlorophosphine; it is crystalline, melts at 142°, and is not decomposed by boiling with water. The *phenylhydrazine salt*, $P(C_{10}H_7O)_2O \cdot ONH_3 \cdot NHPh$, crystallises in long, thin plates, and melts at 183°.   J. B. T.

Chlorophosphines of Bibasic Phenols. By W. KNAUER (*Ber.*, **27**, 2565—2572).—*Resorcinoldichlorophosphine*, $C_6H_4(OPCl_2)_2$, is prepared by the prolonged action of phosphorus trichloride on

resorcinol; it is a colourless, highly refractive liquid, boiling at 240°
(56 mm.); it fumes in air, is violently decomposed by water, even at
low temperatures, and gives a white, unstable compound with chlor-
ine. *Resorcinoldioxychlorophosphine*, $C_6H_4(OPOCl_2)_2$, from resorcinol
and phosphorus oxychloride, is a fuming, colourless, viscid, highly
refractive liquid, boiling at 263° (115 mm.) or at 216° (75 mm.); the
sp. gr. = 1·643 at 15°; it is resolved into resorcinol, hydrogen chlor-
ide, and phosphoric acid by the action of water. *Ethylic resorcinol
diphosphinate*, $C_6H_4[OPO(OEt)_2]_2$, prepared by the action of alcohol
on the preceding compound, is a viscid liquid, and decomposes on
heating, or in presence of water.

Quinoldichlorophosphine resembles the resorcinol derivative in
general properties, and is prepared in a similar manner; it is crystal-
line, melts at 65°, and boils at 200° (65 mm.). *Quinoldioxychloro-
phosphine*, from phosphorus oxychloride and quinol, forms hard,
colourless crystals, melts at 123°, boils at 270° (70 mm.), and, by the
action of alcohol, yields *ethylic quinoldiphosphinate;* it is a yellow
liquid which decomposes when heated.

Secondary catecholchlorophosphine, $C_6H_4{<}^O_O{>}PCl$, prepared by

heating catechol with phosphorus trichloride, forms colourless crystals,
melts at 30°, boils at 140° (65 mm.), and is violently decomposed by
water.

Tertiary catecholphosphine, $C_6H_4{<}^O_O{>}P{\cdot}OC_6H_4O{\cdot}P{<}^O_O{>}C_6H_4$, is

formed together with the preceding compound, from which it is sepa-
rated by fractional distillation; it is a yellow, viscid liquid, boils
above 360° under reduced pressure, and is slowly decomposed by
cold water; its sp. gr. is 1·353 at 15°. *Tertiary catecholphosphine
oxide*, $C_6H_4{<}^O_O{>}PO{\cdot}O{\cdot}C_6H_4{\cdot}O{\cdot}OP{<}^O_O{>}C_6H_4$, is obtained from phos-

phorus oxychloride and catechol as a viscid liquid, boiling above 360°
under diminished pressure; it is hydrolysed by boiling water.

Secondary catecholoxychlorophosphine, $C_6H_4{<}^O_O{>}POCl$, is prepared

by the action of phosphorus oxychloride on the preceding compound;
it crystallises in colourless needles, melts at 35°, boils at 162° (55 mm.),
and is violently decomposed by water.   J. B. T.

Aromatic Oxychlorophosphines. By A. MICHAELIS and G.
SCHULZE (*Ber.*, **27**, 2572—2579; compare this vol., i, 128).—*Diethylic
anilidophosphate*, $NHPh{\cdot}PO(OEt)_2$, is obtained from aniline oxychloro-
phosphine by the action of ethylic alcohol. It forms large, white
plates, which become reddish-yellow in the air and melt at 93°. The
corresponding phenylic salt (Wallach and Heymer, *Ber.*, **8**, 1235) is
obtained by employing phenol; it melts at 129°. *Dicresylic anilido-
phosphate*, $NHPh{\cdot}PO(O{\cdot}C_6H_4Me)_2$, is formed when aniline oxychloro-
phosphine is heated with paracresol (2 mols.) at 220°. The crystal-
line form is hexagonal, and the substance melts at 133°.

When phosphorus oxychloride is heated with aniline (2 mols.)

for 48 hours in a reflux apparatus, dianilineoxychlorophosphine, $(NHPh)_2POCl$, is formed. It melts at 174°, and is unattacked by water and alcohol. Alkalis dissolve it, the solution, when acidified, yielding dianilidophosphoric acid, $PO(NHPh)_2\cdot OH$, in nacreous scales, which melt at 213° (compare Michaelis and v. Soden, Abstr., 1885, 1134). The *copper* salt forms bright blue, anhydrous plates. The *phenylic* salt melts at 125°.

Anilidophosphoric diparatoluidide, $NHPh\cdot PO(NH\cdot C_6H_4Me)_2$, is obtained by adding aniline oxychlorophosphine to fused paratoluidine (4 mols.); it forms silky needles, which melt at 168°. The *trinitro*-compound melts at 220°. *Anilidophosphoric diorthotoluidide* is obtained in a similar manner, and melts at 201°.

Paratoluidineoxychlorophosphine (this vol., i, 128), when treated with ethylic alcohol, gives rise to *diethylic paratoluidophosphate*, $C_6H_4Me\cdot NH\cdot PO(OEt)_2$, which forms colourless, feathery needles and melts at 98°; the *diphenylic* and *dicresylic* salts melt at 134° and 161° respectively.

Dianilidophosphoric paratoluidide, $C_6H_4Me\cdot NH\cdot PO(NHPh)_2$, obtained by the mutual action of paratoluidine, oxychlorophosphine, and aniline (4 mols.), forms short prisms and melts at 168°. *Diparatoluidineoxychlorophosphine*, $POCl(NH\cdot C_6H_4Me)_2$, is deposited from alcohol in small needles, and melts at 210°; when dilute acids are added to its solution, diparatoluidophosphoric acid is formed (compare Rudert, Abstr., 1893, i, 324).

Orthotoluidineoxychlorophosphine, $C_6H_4Me\cdot NH\cdot POCl_2$, melts at 91°; it is readily decomposed by hot water. Alcohol converts it into *diethylic orthotoluidophosphate*, which melts at 95°. The analogous *diphenylic* and *dicresylic* salts melt at 176° and 161° respectively.

Diorthotoluidineoxychlorophosphine, $POCl(NH\cdot C_6H_4Me)_2$, melts at 190°. The alkaline solution, when acidified, yields *diorthotoluidophosphoric acid*, $PO(NH\cdot C_6H_4Me)_2\cdot OH$, which melts at 120°; the *copper* salt crystallises from hot water in bluish-green needles.

Dianilidophosphoric orthotoluidide, $C_6H_4Me\cdot NH\cdot PO(NHPh)_2$, melts at 175°, and crystallises in short, thick prisms. M. O. F.

Paradiacetylbenzene. By H. INGLE (*Ber.*, **27**, 2526—2529; compare A. v. Baeyer, Abstr., 1892, 833).—Ethylic terephthalyldimalonate, $C_6H_4[CO\cdot CH(COOEt)_2]_2$, prepared from terephthalic chloride and ethylic disodiomalonate, crystallises in long, silky needles melting at 110°. It is soluble in soda with a yellow coloration, and is slowly hydrolysed at ordinary temperatures; in alcoholic solution with ferric chloride a cherry coloration is produced. Paradiacetylbenzene (20—30 per cent.), acetylbenzoic acid (30 per cent.), and terephthalic acid (20 per cent.) are formed on heating ethylic terephthalyldimalonate with dilute sulphuric acid. Paradiacetylbenzene, $C_6H_4Ac_2$, crystallises in highly refractive, hexagonal prisms, melts at 114°, and gives no coloration with ferric chloride. The *sodium hydrogen sulphite derivative* is crystalline and melts at 182°. The *phenylhydrazone* crystallises in golden needles, the *dioxime* in colourless needles melting and decomposing at 240°. Acetylbenzoic

acid melts at 205°; the *methylic salt* at 91°; the *phenylhydrazone* crystallises in golden plates melting at 235°; the *oxime* is deposited in plates, and melts at 254°.

Paradi-α-hydroxyethylbenzene, $C_6H_4(CHMe\cdot OH)_2$, is prepared by the reduction of paradiacetylbenzene with sodium amalgam; it is a viscid oil, readily soluble in water and alcohol, decomposes when heated under ordinary pressures, and is not attacked by potassium permanganate in the cold, but, on warming, is oxidised to tere-phthalic acid. Its taste is first sweet, then bitter.

Para-α-bromethyl-α-hydroxyethylbenzene, $CHMeBr\cdot C_6H_4\cdot CHMe\cdot OH$, is obtained by the action of concentrated hydrobromic acid on the preceding compound at ordinary temperatures, and crystallises in colourless needles melting at 136°. *Paradi-α-bromethylbenzene*, $C_6H_4(CHMeBr)_2$, is prepared by the action of hydrogen bromide on paradihydroxyethylbenzene in glacial acetic acid solution; it is crystalline, and melts at 112°.

Paradivinylbenzene is formed by heating the preceding compound with quinoline under reduced pressure; it has an odour resembling that of petroleum, and boils at about 180°, but decomposes when heated under the ordinary pressure. The *tetrabromide*, $C_{10}H_{10}Br_4$, is crystalline, melts at 156·5°, and is converted into paradi-α-bromethylbenzene by the action of hydrogen bromide in glacial acetic acid solution. Attempts to obtain a crystalline nitroso-chloride were unsuccessful.

<div align="right">J. B. T.</div>

Existence of Meta- and Para-iodosobenzoic acid and of Metaiodoxybenzoic acid. By C. WILLGERODT (*Ber.*, **27**, 2326—2337).—Contrary to the statement of Askenasy and Meyer (Abstr., 1893, i, 508) and of Allen (*loc. cit.*, 578), meta- and para-iodosobenzoic acids are easily prepared.

Metaiodosobenzoic acid, $IO\cdot C_6H_4\cdot COOH$, is obtained by cautiously adding caustic soda to an aqueous solution of the iodochloride until the liquid is alkaline, when acid precipitates the iodosobenzoic acid from it; the latter is also formed by the prolonged action of water on the iodochloride. It is an amorphous, yellow substance, and explodes without detonation at 175—180°. If it is covered with water, the latter becomes acid towards litmus, but even after several days the acid retains its yellow colour. The powerful odour characteristic of iodoso-compounds is possessed in a high degree by this acid. It liberates iodine from potassium iodide, and when boiled for some hours with alcohol, the latter is oxidised to aldehyde, and metaiodobenzoic acid is formed. Metaiodosobenzoic acid is but slightly soluble in alcohol and ether, and insoluble in chloroform and benzene; in boiling glacial acetic acid it dissolves, and a yellow, amorphous *substance* is formed, which probably consists of the anhydride. A newly prepared specimen decomposed at 200°, but after some days effervescence took place at 190°. The original acid is soluble in strong sulphuric or in fuming nitric acid, and if boiled with dilute sulphuric acid, yields a partially crystalline mass which is inactive towards potassium iodide.

Metaiodoxybenzoic acid, $IO_2\cdot C_6H_4\cdot COOH$, is formed in association with metaiodobenzoic acid when the foregoing iodoso-compound is

boiled for three hours with water; it is separated by means of its insolubility in boiling glacial acetic acid. It forms yellowish transparent prisms, and detonates at 243°. It dissolves with difficulty in boiling water, the solution depositing brilliant crystals on cooling; the aqueous solution develops in potassium iodide a yellow coloration which gradually deepens, being greatly intensified on the addition of glacial acetic acid. Metaiodoxybenzoic acid is insoluble in alcohol, ether, chloroform, and benzene, and is but slightly soluble in boiling acetic acid; it dissolves in cold caustic soda and in strong sulphuric acid.

Paraiodosobenzoic acid is prepared in a manner similar to that already described for the production of the meta-compound. It is a colourless, amorphous substance possessing the characteristic odour of iodoso-compounds. The point of explosion was found to be either 210°, 212°, or 203—205°, according to the method of preparation. It is insoluble in chloroform, benzene, and alcohol, but dissolves slightly in ether; the aqueous solution liberates iodine from potassium iodide, iodobenzoic acid being formed. Sulphuric and fuming nitric acids dissolve it readily without apparent change.

From a comparison of the properties of the three isomeric iodosobenzoic acids, the author considers that the meta- and para-compounds alone are true carboxylic acids, the ortho-derivative—which does not possess the characteristic odour—probably having the constitution $C_6H_4{<}{{-CO-}\atop{I(OH)}}{>}O$.

<div align="right">M. O. F.</div>

Etherification of the Aromatic Hydroxyl Group. By J. HERZIG (*Ber.*, **27**, 2119—2121).—In connection with the recent observation of Meyer and Sudborough (this vol., i, 463) on the abnormal behaviour of salicylic acid in etherification, the author points out that a similar abnormal behaviour is shown by a number of other substances in which the hydroxyl- and carboxyl-groups are in the ortho-position to one another. It appears, therefore, that in this position the two groups mutually influence one another in such a manner as to partially prevent etherification; the evidence at present available is not, however, sufficient to draw definite conclusions as to the exact nature of the interference which takes place.

<div align="right">H. G. C.</div>

Hexahydroanthranilic and Hexahydrosalicylic acids. By A. EINHORN and A. MEYENBERG (*Ber.*, **27**, 2466—2475).—When anthranilic acid is reduced with sodium in boiling amylic alcohol solution, small quantities of pimelic and hexahydrobenzoic acids are formed, but the main product is *hexahydroanthranilic acid*. This is neutral to litmus, and probably, therefore, has the structure of a betaïne, ${{CH_2 \cdot CH_2 \cdot CH \text{———} NH_3}\atop{CH_2 \cdot CH_2 \cdot CH \cdot CO \cdot O}}$; it melts and decomposes at 274°, and its *copper salt* crystallises with $2H_2O$. Its *ethylic salt* boils at 228—230° (at 148—151° under 30 mm. pressure), and forms a *hydrochloride*, which melts at 156°; if the crude salt is distilled under atmospheric pressure, it is decomposed, probably by the moisture present, into ammonia and Δ^2-tetrahydrobenzoic acid.

When hexahydroanthranilic acid is treated with nitrous acid, it is

converted into *hexahydrosalicylic acid*, identical with the acid obtained
by Dieckmann (succeeding abstract) by reducing ethylic β-ketohexa-
methylenecarboxylate. This acid melts at 111°; its *calcium salt*
crystallises with H_2O; its *barium salt* with $10H_2O$, of which 9 mols.
are lost by efflorescence in the air, the tenth at 130—150°. Its *ethylic
salt* boils at 120—121° under 30 mm. pressure, and, when treated
with Beckmann's reagent (*Annalen*, **250**, 235), yields eventually
ethylic β-ketohexamethylenecarboxylate.   C. F. B.

**Formation of Hexahydrosalicylic acid by Reduction of
Ethylic β-Ketohexamethylenecarboxylate.** By W. DIECKMANN
(*Ber.*, **27**, 2475—2477).—Hexahydrosalicylic acid is obtained by re-
ducing ethylic β-ketohexamethylenecarboxylate (this vol., i, 173)
with sodium amalgam. It is identical with the acid described by
Einhorn and Meyenberg (last abstract).   A. R. L.

Oxylactones derived from Phenylpyruvic acid. By C. ERLEN-
MEYER, jun., and N. KNIGHT (*Ber.*, **27**, 2222—2226).—When phenyl-
pyruvic acid is boiled with dilute sulphuric acid, a neutral substance
of the formula $C_{17}H_{14}O_3$, is formed. In this reaction, a portion of the
phenylpyruvic acid is decomposed with elimination of carbonic
anhydride, whilst the remainder reacts with the phenylacetaldehyde
thus produced to form the new compound, which is an oxylactone,

$$CH_2Ph \cdot CH {\displaystyle \diagdown_{O \underline{\quad\quad} CO}^{CHPh \cdot CO}}$$ The same compound is formed during the

preparation of phenylpyruvic acid from α-benzoylamidocinnamic acid
(Plöchl, *Ber.*, **16**, 2878), and when ethylic phenylcyanopyruvate is
heated with sulphuric acid. It forms a *sodium* compound, which
dissolves readily in absolute alcohol, and is soluble in hot ether,
but only very sparingly in water, forming a solution which is
decomposed on boiling, phenylpyruvic acid and phenylacetaldehyde
being formed. The sodium compound has a strongly alkaline reac-
tion, and still contains the unbroken lactone ring. The *methyl-*
derivative, $C_{18}H_{16}O_3$, prepared from the sodium compound, melts at
102°, whilst the *benzyl-*derivative crystallises in splendid prisms, and
melts at 67°. Both these compounds contain the lactone ring. The
lactone itself gives a green coloration with ferric chloride, whilst
the methylic derivative does not.

Benzaldehyde condenses with phenylpyruvic acid in a similar

manner, forming an oxylactone, $CHPh {\displaystyle \diagdown_{CO \underline{\quad\quad} CO}^{CHPh \cdot O}}$, which crystal-

lises in white needles, and melts at 206°.   A. H.

Ethylic Phenacylcyanacetates. By T. KLOBB (*Compt. rend.*,
119, 161—162).—When ethylic sodiocyanacetate in alcoholic solution
is mixed, in molecular proportion, with bromacetophenone, dissolved
in three times its weight of dry ether, two products are formed,
and may be separated by means of the difference in their solubilities
in ether. *Ethylic diphenacylcyanacetate*, $COOEt \cdot C(CN)(CH_2 \cdot COPh)_2$,
crystallises from boiling alcohol in white needles, melts at 142°,
and is only slightly soluble in most solvents. *Ethylic phenacylcyan-*

acetate, COOEt·CH(CN)·CH₂·COPh, is formed in smaller proportion, and is more difficult to purify. It crystallises from alcohol in white leaflets melting at 54°, and is also soluble in ether.

The lower homologues can be prepared from methylic cyanacetate in a similar manner. *Methylic diphenacylcyanacetate* forms microscopic needles, which melt at 195°, and are insoluble in ether, and only slightly soluble in boiling alcohol or benzene. *Methylic phenacyl-cyanacetate* crystallises from ether in nodules, and from alcohol in long needles; it melts at 54°, and is very soluble in the ordinary solvents.

The phenacylcyanacetates acquire a yellow colour in contact with an aqueous solution of potassium hydroxide, and the addition of an acid to the alkaline solution produces a blue precipitate. The diphenacylcyanacetates dissolve in alcoholic potash with formation of a deep blue solution, which yields a red precipitate when acidified.

C. H. B.

Ethylic Terephthalodicyanacetate. By J. Locher (*Compt. rend.*, **119**, 162—165).—Terephthalic chloride can conveniently be prepared by heating together for several hours in a flask fitted with a reflux condenser terephthalic acid (1 mol.), phosphorus pentachloride (3½ mols.), and phosphorus oxychloride (3 mols.), allowing the liquid to remain for about 12 hours, and separating and fractionating the liquid portion.

Dry and finely-powdered ethylic sodiocyanacetate (4 mols.) suspended in four times its weight of dry ether, is mixed with terephthalic chloride (1 mol.) dissolved in twice its weight of ether, and the mixture is gently heated. After 24 hours, the mixture is filtered, and the insoluble product washed with warm ether, dissolved in water, and mixed with acetic acid, which precipitates *ethylic terephthalocyanacetate*. The latter, purified by crystallisation from alcohol, forms long, white needles, which melt at 179°. It is insoluble in water, but dissolves in most organic solvents, and also in solutions of alkali carbonates or hydroxides, and in ammonia. It decomposes when heated at 100°, or when boiled with water or solutions of alkalis. With ferric chloride, the sodium salt gives the red colour which, according to Haller, is characteristic of the group CN·CO·CH·COOEt.

Ethylic terephthalocyanacetate is a true bibasic acid. Its copper salt is a green crystalline powder containing 2H₂O; the lead salt is white and amorphous; the di-silver salt is white and amorphous, and blackens when exposed to light; the ammonium salt is white and amorphous.

When boiled with water, ethylic terephthalocyanacetate splits up into terephthalic acid and ethylic cyanacetate, and does not yield a derivative analogous to cyanacetophenone. Sodium carbonate or sodium hydroxide produces a similar result. When boiled for two hours with phenylhydrazine (2 mols.), in presence of chloroform, it yields a hydrazone, C₆H₄[C(N₂HPh)·CH(CN)·COOEt]₂, which crystallises from absolute alcohol in colourless crystals, melting at 260—261°; it is insoluble in water, and only slightly soluble in other solvents.

C. H. B.

Action of Sodium Ethoxide on Benzaldehyde and Ethylic Succinate. By H. STOBBE and E. KLOEPPEL (*Ber.*, **27**, 2405—2409).— Benzaldehyde reacts much in the same manner as acetone (this vol., i, 15), when it (2 mols.) is mixed with ethylic succinate (1 mol.) in ethereal solution and sodium ethoxide (2 mols.) is added to the cooled solution. An acid, probably

$$CHPh:C(COOH)\cdot C(COOH):CHPh,$$
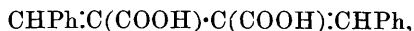
melting and decomposing at 201°, is obtained; and, in addition, a mixture of phenylitaconic acid, $COOH\cdot CH_2\cdot C(COOH):CHPh$, with some isomeric phenylaticonic acid (Fittig, 1890, 894; Abstr., 1893, i, 691).   C. F. B.

Substituted Isoimides of Phthalic acid. By S. HOOGEWERFF and W. A. VAN DORP (*Rec. Trav. Chim.*, **13**, 93—100; compare Abstr., 1893, i, 599).—*Phthalomethylisoimide,* $C_6H_4{<}^{C(NMe)}_{CO}{>}O$, prepared by heating phthalomethylamic acid with acetic chloride, is deposited from a mixture of ether and light petroleum in stellate crystals, and melts at 76·5—78·5°. Phthalomethylimide melts at 132°. The isomeride is a base, but its salts readily decompose in presence of water, forming phthalomethylamic acid.

Phthalobenzylisoimide, $C_6H_4{<}^{C(NC_7H_7)}_{CO}{>}O$, prepared in a similar manner from phthalobenzylamic acid, forms colourless crystals. melts at 81—82·5°, and resembles the methyl derivative in general properties.

Non-substituted isoimides have not yet been isolated, but impure hydrochlorides have been prepared and also *camphorisoimide auro-chloride,* $C_8H_{14}{<}^{C(NH)}_{CO}{>}O,HAuCl_4$. In addition to the arguments previously advanced in favour of the constitution of the isomerides given above (*loc. cit.*), another is afforded by a comparison of their properties with those of acetamide and diacetamide; the basic properties of the isoimides preclude the presence of the group $CO\cdot NH\cdot CO$. Phthalomethylamic acid and phthalobenzylamic acid are readily prepared by dissolving phthalic anhydride in aqueous solution of methylamine or benzylamine and acidifying with hydrochloric acid.

A second camphormethylisoimide and two camphorisoimide hydrochlorides which give two acids of the formula $CN\cdot C_8C_{14}\cdot COOH$, have also been prepared, and will be described later. Their formation indicates that the carboxyl-groups in camphoric acid are unsymmetrical.   J. B. T.

Action of Thionyl Chloride on Organic Compounds. By F. LOTH and A. MICHAELIS (*Ber.*, **27**, 2540—2548).—Thionyl chloride and anisoïl, in presence of aluminium chloride, combine to form *thiomethoxybenzene,* $S(C_6H_4\cdot OMe)_2$, which crystallises from benzene in colourless plates, melts at 46°, and is also formed from anisoïl

and sulphur monochloride or dichloride, and from thionyl chloride and mercuric dimethoxybenzene. *Tetrabromothiomethoxybenzene,* $S(C_6H_2Br_2\cdot OMe)_2$, is prepared by the action of bromine in glacial acetic acid on thiomethoxybenzene, and crystallises in colourless needles melting at 132°. Parabromochloromethoxybenzene, $C_6H_3BrCl\cdot OMe$, is produced by the interaction of thionyl chloride and parabromomethoxybenzene.

Thiomethoxybenzene and tetrabromomethoxybenzene, on oxidation with nitric acid (sp. gr. 1·3) yield *thionylmethoxybenzene,*

$$SO(C_6H_4\cdot OMe)_2,$$
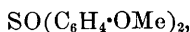
and *thionyltetrabromomethoxybenzene,* $SO(C_6H_2Br_2\cdot OMe)_2$, respectively; the former crystallises in transparent, pale yellow rhombohedra melting at 96°, the latter in pale, lustrous plates melting at 155°; it could not be obtained by the direct action of bromine on thionylmethoxybenzene. *Methoxybenzenesulphone,* $SO_2(C_6H_4\cdot OMe)_2$, is formed by the oxidation of thiomethoxybenzene with potassium permanganate; it crystallises in lustrous, transparent needles, and melts at 120°. The *bromo-derivative,* $OMe\cdot C_6H_4\cdot SO_2\cdot C_6H_3Br\cdot OMe$, is deposited in pearly plates melting at 170°.

The following ethoxy-derivatives were prepared in a similar manner to the corresponding methoxy-compounds. *Thio-thoxybenzene,* $S(C_6H_4\cdot OEt)_2$, is deposited from benzene in colourless, quadratic crystals melting at 55°. The yield is 40 per cent. of the phenetoïl employed. *Tetrabromothioethoxybenzene,* $S(C_6H_2Br_2\cdot OEt)_2$, crystallises in needles, and melts at 142°. *Thionylethoxybenzene* crystallises in transparent rhombohedra melting at 116°. *Ethoxybenzenesulphone* is deposited in thin, lustrous plates, and melts at 263°. The *bromoderivative,* $OEt\cdot C_6H_4\cdot SO_2\cdot C_6H_3Br\cdot OEt$, crystallises in milky plates, and melts at 185°.

Thionyl chloride acts directly on α-methoxynaphthalene and α-ethoxynaphthalene, whilst the β-derivatives require the presence of aluminium chloride; in all cases thio-derivatives are formed. *Thio-α-methoxynaphthalene,* $S(C_{10}H_6\cdot OMe)_2$, crystallises from chloroform in well-developed rhombohedra melting at 135°. *Thio-α-ethoxynaphthalene,* $S(C_{10}H_6\cdot OEt)_2$, forms lustrous, transparent crystals; it melts at 153°, and is sparingly soluble in chloroform. *Thio-β-methoxynaphthalene* crystallises in pearly, transparent plates. *Thio-β-ethoxynaphthalene* is deposited in lustrous crystals melting at 195°. By the action of nitric acid on the preceding naphthalene derivatives, crystalline compounds free from sulphur are formed. Chromic acid and alkaline potassium permanganate do not act on them, but on treatment with potassium permanganate in presence of glacial acetic acid two compounds are obtained, one crystallises in small, red needles and melts at 232°, whilst the other forms colourless needles, melts at 167°, and is probably either the sulphone of a thionaphthol ether, $SO_2:(C_{10}H_6)_2:O$, or a sulphur derivative of naphthaquinone. Dark, amorphous products are formed by the action of bromine on the thionaphthol ethers.

With thionylbenzene, thionyl chloride reacts like phosphoric chloride, forming chlororthothiobenzene, $C_6H_4Cl\cdot SPh$, hydrogen

chloride, and sulphurous anhydride; with thionyl chloride in excess at higher temperatures, dichlororthothiobenzene is obtained.

Bromochlororthothiobenzene is prepared by the action of bromine on chlororthothiobenzene dissolved in glacial acetic acid; it crystallises in lustrous, stellate plates, and melts at 110°. By the action of chlorine under similar conditions, di-, tri-, and tetra-chlororthothiobenzenes are formed.

Benzaldehyde and thionyl chloride react to form benzal chloride. Sulphur monochloride does not act on benzaldehyde at ordinary temperatures; at 150°, benzoic chloride, sulphur, and hydrogen chloride are formed; in presence of aluminium chloride at ordinary temperatures, tarry substances are produced.

Thionyl chloride and acetone react violently, sulphurous anhydride and hydrogen chloride are evolved, and mesitylic oxide is formed, together with a disagreeably-smelling oil, which decomposes on distillation. Acetoxime and thionyl chloride react to form an unstable oily compound, which probably has the formula $SO(NO{:}CMe_2)_2$. No crystalline compounds could be obtained by the interaction of thionyl chloride and acetophenone. J. B. T.

Thionyl Derivatives of Substituted Phenylhydrazines and of Hydrazinebenzoic acids. By J. KLIEEISEN (*Ber.*, **27**, 2549—2556). —It has been shown by Michaelis and his pupils that aromatic hydrazines and ethylic metamidobenzoate react with thionyl chloride, the thionyl radicle displacing the hydrogen of the amido-group, but that metamidobenzoic acid does not form a thionylamine.

Metanitrothionylphenylhydrazone, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}SO$, is prepared from metanitrophenylhydrazine hydrochloride and thionylaniline in presence of sodium acetate at ordinary temperatures, and crystallises in slender, pale yellow needles melting at 185°; it is not altered by boiling water; with hot soda, a red coloration is produced, probably due to the formation of a *sodium salt*. At ordinary temperatures, it dissolves in soda with a yellow colour, which soon disappears, nitrophenylhydrazine being simultaneously deposited. By the action of bromine on the thionylhydrazone, metanitrodiazobenzene perbromide, $NO_2{\cdot}C_6H_4{\cdot}N_2Br_3$, is formed. Thionyl chloride and the thionylhydrazone do not react at ordinary temperatures, but on warming metanitrodiazobenzene chloride is produced. Attempts to reduce the thionylhydrazone were unsuccessful. *Orthonitrothionylphenylhydrazone* resembles the meta-compound, and is prepared in a similar manner; it crystallises in small, red plates, melts at 128°, and does not yield diazo-derivatives by the action of bromine or thionyl chloride. *Orthonitrophenylhydrazine phosphite*,

$$(NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2)_2H_3PO_3,$$
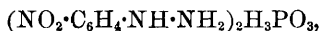
crystallises in large, canary-coloured needles, and melts at 160°. *Parachlorothionylphenylhydrazone*, $C_6H_4Cl{\cdot}NH{\cdot}N{:}SO$, prepared in a similar manner to the nitro-compound, crystallises in slender, greenish-yellow needles, and melts at 159°. By the action of bromine, it yields parachlorodiazobenzene perbromide, and, by treatment with thionyl chloride, parachlorodiazobenzene chloride. *Parabromothionyl-*

phenylhydrazone, $C_6H_4Br\cdot NH\cdot N\dot{:}SO$, is prepared in a similar manner to the chloro-derivative, which it closely resembles in properties and reactions. It crystallises in small, yellow needles melting at 168°. *Dibromothionylphenylhydrazone*, $C_6H_3Br_2\cdot NH\cdot N\dot{:}SO$, is prepared from thionylaniline and dibromophenylhydrazine, and crystallises in long, transparent, yellow, stellate needles melting at 99°. It readily sublimes, does not react with thionyl chloride or phosphorus chloride, and yields dibromodiazobenzene perbromide by the action of bromine. *Parabromorthonitrothionylphenylhydrazone*, $NO_2\cdot C_6H_3Br\cdot NH\cdot N\dot{:}SO$, prepared in a similar manner to the preceding compound, forms small, pale yellow crystals, melts at 157°, and is converted into the corresponding diazo-derivative by the action of bromine and thionyl chloride.

Metathionylhydrazinebenzoic acid, $COOH\cdot C_6H_4\cdot NH\cdot N\dot{:}SO$, formed from metahydrazinebenzoic acid and thionylaniline, crystallises in small, yellow plates, melts at 231°, and explodes when heated in a test-tube. It dissolves and decomposes in alkalis and alkali carbonates, and yields the diazoperbromide and diazochloride by the action of bromine and thionyl chloride respectively. *Parathionylhydrazinebenzoic acid* forms small, yellow crystals melting at 258°. *Orthothionylhydrazinebenzoic acid* crystallises in long, pale yellow needles, melts at 152°, and explodes at 155°, forming sulphurous anhydride and orthohydrazinebenzoic anhydride. Both the ortho- and para-compounds resemble the meta-derivatives in their properties and mode of formation. Attempts to prepare salts of these acids were unsuccessful. J. B. T.

The Two Isomeric Forms of Diazobenzene Potassium Sulphite. By A. CLAUS (*J. pr. Chem.*, [2], **50**, 239—240).—These two compounds, supposed by Hantzsch (this vol., i, 455) to be stereoisomeric only, the author regards as structurally isomeric. The orange-red unstable substance is diazobenzene potassiumsulphonate, $K\cdot SO_2\cdot O\cdot N_2Ph$; the yellow stable one, potassium diazobenzenesulphonate, $N_2Ph\cdot SO_2\cdot OK$. C. F. B.

Stereoisomerism of the Benzenediazosulphonic Salts. By A. HANTZSCH (*Ber*, **27**, 2099—2102).—E. Fischer suggested privately to the author the view of the constitution of these salts that has since been published by Claus (preceding abstract). This view is now discussed and rejected, the original (this vol., i, 453, 455) stereoisomeric formulæ being preferred. C. F. B.

Partial Diazotisation of Benzidine. By E. TÄUBER (*Ber.*, **27**, 2627—2631).—4 : 4'-*Amidodiazodiphenyl choride*,

$$NH_2\cdot C_6H_4\cdot C_6H_4\cdot N\dot{:}NCl,$$
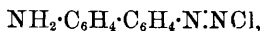
is obtained by mixing together solutions of tetrazodiphenyl chloride and benzidine hydrochloride in molecular proportion, and allowing the mixture to remain at 10—20° for two or three days. On boiling the solution, 4 : 4'-*hydroxyamidodiphenyl* is formed ; it melts at 273°, and the most suitable solvents for crystallisation are alcohol and aniline. The *acetyl*-derivative melts at 225°, and when the alcoholic solution

of this substance is heated with ethylic bromide and caustic potash, 4 : 4'-*ethoxyacetamidodiphenyl*, $OEt \cdot C_6H_4 \cdot C_6H_4 \cdot NHAc$, is produced. It forms colourless needles which melt at 210° and its physiological action is comparable with that of phenacetin.   M. O. F.

Symmetrical Diamidoacridone. By M. Schöpff (*Ber.*, **27**, 2316—2321).—*Diamidoacridone*, $NH_2 \cdot C_6H_3 <^{NH}_{CO}> C_6H_3 \cdot NH_2$, is prepared by reducing tetranitrobenzophenone with stannous chloride and hydrochloric acid ; the *stannochloride* is first formed, separating in fine, reddish-brown needles, which on prolonged warming with water yield metastannic acid and diamidoacridone hydrochloride in almost quantitative amounts. The base forms colourless needles, the melting point of which is not reached at 350°. The alcoholic solution exhibits bluish-violet fluorescence; the solution in phenol is yellow with green fluorescence, which is also shown by dilute solutions of the base in mineral acids. The *dihydrochloride* readily loses hydrogen chloride with formation of the *monohydrochloride*, $C_{13}H_{11}N_3O,HCl + 4H_2O$, which separates from the aqueous solution of the normal salt in yellowish needles, the dilute solution of which exhibits a bluish-green fluorescence. *The platinochloride* forms microscopic orange needles. Symmetrical *diamidoacridine*, $NH_2 \cdot C_6H_3 <^{N-}_{CH}> C_6H_3 \cdot NH_2$, is obtained by reducing diamidoacridone in alcoholic solution with sodium; it forms yellow needles which melt at 281°.   M. O. F.

Stereoisomerides of Carbodiphenylimide and Carboditolylimides. By C. Schall (*Ber.*, **27**, 2260—2263; compare Abstr., 1892, 1452; this vol., i, 135). The author maintains his view that α- and β-carbodiphenylimide and α- and β-carboditolylimide are stereoisomerides, against the criticism of Miller and Plöchl (*Ber.*, **26**, 1283). The two derivatives have the same molecular weight in benzene solution, and, therefore, are not polymerides.   A. H.

Diphenols. By C. Haeussermann and H. Teichmann (*Ber.*, **27**, 2107—2109).—The diphenol melting at 123·5°, obtained with other products when phenol is fused with potash, is shown to be 3 : 3'-*dihydroxydiphenyl*, $C_{12}H_8(OH)_2$. This substance was prepared both from orthodianisidine by removing the amido-groups and hydrolysing the resulting dimethylic ether, and from 3 : 3'-diamidodiphenyl by the diazo-reaction. It forms a *dimethyl*- and a *diacetyl-derivative* which melt at 36° and at 82·5° respectively.   C. F. B.

Action of Ethylic Sodiomalonate on Benzalacetone. By A. Michael (*Ber.*, **27**, 2126—2130).—By the action of an ethereal solution of benzalacetone on ethylic sodiomalonate suspended in ether, a yellowish crystalline sodium salt is obtained, which on treatment with acids yields an ethylic salt having the composition $C_{15}H_{14}O_4$: this crystallises in small needles or prisms, melts at 144—145°, and yields a hydrazone crystallising in microscopic four-

sided colourless plates, which redden in the air. On treatment with hot potash, it undergoes hydrolysis and simultaneously loses carbonic anhydride, yielding the compound $C_{12}H_{12}O_2$, which forms quadratic plates melting at 183—185°. These compounds are identical with those obtained by Michael and Freer (Abstr., 1891, 914) by the action of ethylic cinnamate on ethylic sodacetoacetate, but the new synthesis is not in agreement with the constitutional formulæ previously assigned to them, which must, therefore, be abandoned. The most probable supposition is that they are derivatives of hexamethylene, the compounds $C_{15}H_{16}O_4$ and $C_{12}H_{12}O_2$, having the following constitutional formulæ :—

$$\begin{array}{cc} \text{CHPh·CH}_2\text{·CO} & \text{CHPh·CH}_2\text{·CO} \\ \text{COOEt·CH·CO——CH}_2 & \text{CH}_2\text{·CO——CH}_2 \end{array}$$

and
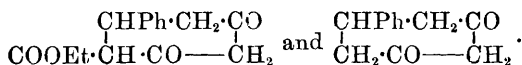
The latter compound is, on this assumption, a *phenyldihydroresorcinol,* and therefore corresponds with Merling's dihydroresorcinol, the diketone formula of which the author regards as more probable than Merling's (this vol., i, 177). H. G. C.

Derivatives of Diphenylmethane and of Benzophenone. By W. STAEDEL (*Ber.,* **27,** 2109—2111).—2-Nitrodiphenylmethane when nitrated yields 2 : 4'-dinitrodiphenylmethane, melting at 118°, hitherto known as δ-dinitrodiphenylmethane. 4-Nitrodiphenylmethane yields 4 : 4'-dinitrodiphenylmethane (α) melting at 183°, together with some of the 2 : 4' (δ) isomeride. 3-Nitrodiphenylmethane yields 3 : 4'-dinitrodiphenylmethane, melting at 101—102°.

These diphenylmethane derivatives can be oxidised to the corresponding derivatives of benzophenone. Of the latter, 2-nitrobenzophenone, when nitrated, yields 2 : 2'-dinitrobenzophenone (γ) melting at 188°, and convertible into xanthone, together with less of the 2 : 3' (ε) isomeride, melting at 126°. 4-Nitrobenzophenone yields a mixture of 4 : 4' (α), 4 : 2' (δ), and 4 : 3'-dinitrobenzophenone, melting respectively at 189°, 196°, and 172° ; the last of these is a new substance. 3-Nitrobenzophenone yields 3 : 3'-dinitrobenzophenone (β) melting at 148—149°, together with small quantities of the 3 : 2' (ε) and 3 : 4' isomerides. C. F. B.

Condensation of Aromatic Alcohols with Nitro-hydrocarbons. By L. GATTERMANN and H. RÜDT (*Ber.,* **27,** 2293—2297).—2 : 4'-*Dinitrodiphenylmethane,* $CH_2(C_6H_4 \cdot NO_2)_2$, is obtained when paranitrobenzylic alcohol or paranitrobenzylic acetate is heated with nitrobenzene and concentrated sulphuric acid in an oil bath for $1\frac{1}{2}$ hours at 130—140°. It crystallises in long, silky, colourless needles, and melts at 103—104°. When reduced, it is converted into 2 : 4'-*diamidodiphenylmethane;* this crystallises in lustrous leaflets, melts at 89—90°, and turns brown on exposure to air.

2 : 4'-*Dinitrobenzophenone,* $CO(C_6H_4 \cdot NO_2)_2$, is obtained by oxidising dinitrodiphenylmethane with chromic anhydride in acetic acid solution. It crystallises in stout, pale yellow needles, and melts at 175°. The 2 : 4'-*diamidobenzophenone* obtained from it by reduction, crys-

tallises in yellow prisms containing alcohol, which melt at 104°, and, atter drying on the water bath, at 121—122°. The *diacetyl-derivative* crystallises in white needles and melts at 218°.

3 : 4'-*Dihydroxybenzophenone*, obtained from the amido-compound by means of the diazo-reaction, crystallises in colourless needles, and melts at 200°.

3 : 3'-*Dinitrodiphenylmethane*, obtained in a similar way to the 2 : 4'-compound, crystallises in small leaflets, and melts at 172°. The dinitrobenzophenone obtained from it melts at 151°; the diamido-benzophenone crystallises in golden yellow needles and melts at 173—174°, and the dihydroxybenzophenone melts at 163—164°. These benzophenone derivatives are identical with those obtained by the nitration of benzophenone.

Dinitrophenyltolylmethane, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3Me \cdot NO_2$ [$CH_2 : NO_2$ = 1 : 4 ; $CH_2 : Me : NO_2$ = 1 : 3 : 4], obtained from paranitrobenzylic acetate and orthonitrotoluene, crystallises in long, white needles, and melts at 143°.

Phenylnitrotolylmethane, $CH_2Ph \cdot C_6H_3Me \cdot NO_2$, obtained from metanitrobenzylic alcohol and orthonitrotoluene, crystallises in nacreous leaflets, and melts at 139—140°. E. C. R.

Condensation with Formaldehyde. By M. Schöpff (*Ber.*, **27**, 2321—2326).—3 : 3'-*Dinitrodiphenylmethane* (m. p. 174°) is formed under certain conditions when formaldehyde is heated with nitrobenzene and sulphuric acid (D.R.P., 67,001). On reduction, it yields 3 : 3'-*diamidodiphenylmethane*, which melts at 47—48°.

Compounds resulting from the condensation of formaldehyde with ortho-, meta-, and paranitrophenols have already formed the subject of various patents (D.R P., 72,490, 73,946, and 73,951), whilst from metanitrodimethylaniline is obtained dinitrotetramethyldiamidodiphenylmethane [$NMe_2 : NO_2 : CH_2 = 1 : 3 : 4$]. Employing benzoic acid, *diphenylmethane-3 : 3'-dicarboxylic acid* is formed, soluble with difficulty in water, more easily in methylic and ethylic alcohols, the solutions exhibiting green fluorescence, which is also shown when acetone or glacial acetic acid is the solvent; it melts at 220—225°. For purposes of comparison, *diphenylmethane-4 : 4'-dicarboxylic acid* was prepared, and is found to melt at 290°. It is formed on hydrolysing 4 : 4'-*dicyanodiphenylmethane*, which may be obtained in large crystals melting at 165°. The solution in benzene is characterised by a green fluorescence. M. O. F.

Condensation Products of Orthoaldehydic Acids with Phenols. By A. Bistrzycki and G. J. Oehlert (*Ber.*, **27**, 2632—2640).—*Hydroxyphenylphthalide*, $\begin{smallmatrix} C_6H_4 \\ CO \cdot O \end{smallmatrix} > CH \cdot C_6H_4 \cdot OH$, is obtained by the condensation of phthalaldehydic acid with phenol in the presence of strong sulphuric acid. It melts at 148—151°, and yields anthracene when distilled with zinc dust. The *nitro*-compound melts at 152—153°, and the *dibromo*-derivative at 223—224°. The *acetyl*-derivative melts at 125—126·5°.

Metacresylphthalide, $\underset{CO\cdot O}{\overset{C_6H_4}{\big|}}$>$CH\cdot C_6H_3Me\cdot OH$, is prepared in the same way as the foregoing phthalide; it melts at 169—170°.

Resorcylphthalide, $\underset{CO\cdot O}{\overset{C_6H_4}{\big|}}$>$CH\cdot C_6H_3(OH)_2$, separates from dilute alcohol in fine, colourless needles, which lose 1 mol. H_2O at 120°, and melt at 130°. The *dibromo*-derivative melts at 197·5—199·5°.

Orcylphthalide, $\underset{CO\cdot O}{\overset{C_8H_4}{\big|}}$>$CH\cdot C_6H_3Me(OH)_2$, forms small, colourless plates, and melts at 241—242°, whilst *pyrogallylphthalide,*

$$\underset{CO\cdot O}{\overset{C_6H_4}{\big|}}>CH\cdot C_6H_2(OH)_3,$$
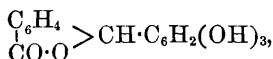
melts at 175—177°.

The employment of opianic acid in place of phthalaldehydic acid gives rise to meconin-derivatives; nitro- and bromopianic acids, however, do not condense with phenol.

Hydroxyphenylmeconin, $\underset{CO \underline{\quad\quad} O}{\overset{C_6H_2(OMe)_2}{\big|}}$>$CH\cdot C_6H_4\cdot OH$, crystallises in nodular aggregates of needles, and melts at 160—170°; the *nitro*-compound melts at 177·5—179°, and the *dibromo*-derivative crystallises from glacial acetic acid in fine needles, melting at 195·5—196·5°.

Metacresylmeconin, $\underset{CO \underline{\quad\quad} O}{\overset{C_6H_2(OMe)_2}{\big|}}$>$CH\cdot C_6H_3Me\cdot OH$, is microcrystalline.

M. O. F.

Derivatives of Benzoylbenzoic Acid. By A. HALLER and A. GUYOT (*Compt. rend.*, 119, 139—142).—When phosphorus pentachloride is added to a carbon bisulphide solution of benzoylbenzoic acid, prepared by Friedel and Craft's method, there is an energetic action with evolution of hydrogen chloride and formation of a brown, oily liquid, which decomposes readily into benzoylbenzoic acid and hydrogen chloride. If this liquid is dissolved in benzene, and aluminium chloride is added to the solution, diphenylphthalide is obtained. It would follow that the product of the action of phosphorus pentachloride is $C_6H_4<\underset{-\;CO\;-}{\overset{CClPh}{\big|}}>O$. Moreover, this view is supported by the fact that if in the preparation of diphenylphthalide from phthalic chloride, an insufficient quantity of aluminium chloride is added, benzoylbenzoic acid is also formed.

Dimethylamidodiphenylphthalide, $\underset{COO}{\overset{C_6H_4}{\big|}}$>$CPh\cdot C_6H_4\cdot NMe_2$, is obtained by adding gradually to a solution of benzoylbenzoic acid in a large excess of dimethylaniline, the calculated quantity of phosphorus trichloride also dissolved in dimethylaniline, the temperature of the liquid not being allowed to rise above 50°. It crystallises from alcohol in white crystals, which melt at 119° and dissolve in most organic solvents, especially on heating. It combines with acids, and the hydrochloride forms white plates which lose their hydrochloric acid at 100° and dissociate readily in contact with water.

Dimethylamidotriphenylmethanecarboxylic acid,

$$COOH \cdot C_6H_4 \cdot CHPh \cdot C_6H_4 \cdot NMe_2,$$

is obtained quantitatively by the action of zinc on a hydrochloric
acid solution of the phthalide, or better by the action of sodium
amalgam on an alcoholic solution. It crystallises from xylene in
small, white crystals, which melt at 190° and are only slightly soluble
in ordinary solvents.

Dimethylamidophenylanthranol, $C_6H_4 <^{C(C_6H_4 \cdot NMe_2)}_{C(OH)} ---->C_6H_4,$ or

$C_6H_4 <^{CPh(C_6H_4)}_{C(OH)} ->C_6H_3 \cdot NMe_2,$ formed when the preceding com-
pound is triturated with concentrated sulphuric acid, is a yellow
powder which crystallises from boiling xylene in long, golden-yellow
needles; it decomposes before it melts.   C. H. B.

Amidobenzoylbenzoic acids and Dimethylanilinephthaleïn.

By A. HALLER and A. GUYOT (*Compt. rend.*, 119, 205—207).—If, in
the preparation of benzoylbenzoic acid (preceding abstract) dimethyl-
aniline is employed in place of benzene, the product is dimethyl-
amidobenzoic acid. The dimethylaniline must be dissolved in carbon
bisulphide in order to avoid its decomposition by the aluminium
chloride. The product is dissolved in dilute sulphuric acid, repre-
cipitated with ammonia, and purified by dissolution in sodium carbon-
ate and crystallisation from alcohol.

Dimethylamidobenzoylbenzoic acid forms yellow, acicular or lozenge-
shaped crystals which melt at 199°. It combines with acids and bases,
forming two series of salts, which are generally readily crystallisable.
The *sodium salt*, $COONa \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot NMe_2$, or

$$^{C_6H_4}_{CO \cdot O} > C(ONa) \cdot C_6H_4 \cdot NMe_2,$$
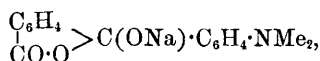
forms white crystals, soluble in water and alcohol, and when treated
with sulphuric acid yields the original acid. The *methylic salt* is
formed quantitatively when a solution of the acid in methylic alcohol
is saturated with hydrogen chloride; it forms large, white crystals
melting at 128°, soluble in all ordinary solvents, and regenerating the
yellow acid when hydrolysed. The formation of this ethereal salt
would seem to indicate that the dimethylamidobenzoylbenzoic acid
has a carboxylic function.

The dimethylanilinephthaleïn obtained by Fischer by the action of
phthalic anhydride or phthalic chloride on dimethylaniline in presence
of zinc chloride, can easily be prepared by the action of phosphorus
chloride on a mixture of dimethylaniline and dimethylamidobenzoic
acid, the yield being 90 per cent. of the calculated quantity.

Methylic tetramethyldiamidotriphenylmethanecarboxylate,

$$COOMe \cdot C_6H_4 \cdot CH(C_6H_4 \cdot NMe_2)_2,$$

is obtained by the action of hydrogen chloride on a solution in
methylic alcohol of the acid obtained by the reduction of dimethyl-

anilinephthaleïn with zinc and hydrochloric acid. It forms beautiful, white crystals, only slightly soluble in alcohol or ether, but much more soluble in chloroform, especially on heating. The salts usually crystallise well. The zincochloride crystallises from alcohol in white prisms.

Diethylamidobenzoylbenzoic acid and its derivatives are obtained in a similar manner by substituting diethylaniline for dimethylaniline, and they have the same general properties. The acid forms yellowish crystals melting at 180°. *Diethylanilinephthaleïn* crystallises in needles. C. H. B.

Ortho-α-tricyanodibenzyl. By S. GABRIEL and T. POSNER (*Ber.*, **27**, 2492—2506).—The authors have improved the method of preparing ortho-α-tricyanodibenzyl (this vol., i, 279). When the tricyano-derivative is heated with hydrobromic acid of sp. gr. 1·47, the chief portion of the product consists of *dibenzylortho-α-tricarboxylimide (α-benzylhomophthalimidorthocarboxylic acid)*,

$$\begin{matrix} NH-CO \\ | \\ CO \cdot C_6H_4 \end{matrix} > CH \cdot CH_2 \cdot C_6H_4 \cdot COOH \; ;$$
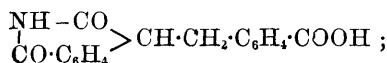
this crystallises in white, microscopic, flat needles, melts at 242°, and dissolves in ammonia with an intense yellow coloration. If boiled with acetic anhydride, the *anhydro*-compound,

$$\begin{matrix} NH-CO \\ | \\ CO \cdot C_6H_4 \end{matrix} > C < \begin{matrix} CO \\ CH_2 \end{matrix} > C_6H_4,$$
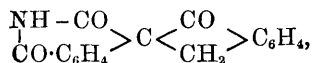
is formed; it melts at 263°. When dibenzylortho-α-tricarboxylic imide is heated with methylic alcohol, potash and methylic iodide, it yields *methylic α-methyldibenzylorthotricarboxylmethylimide*,

$$\begin{matrix} NMe \cdot CO \\ | \\ CO \cdot C_6H_4 \end{matrix} > CMe \cdot CH_2 \cdot C_6H_4 \cdot COOMe,$$
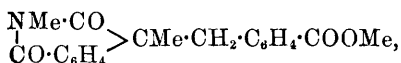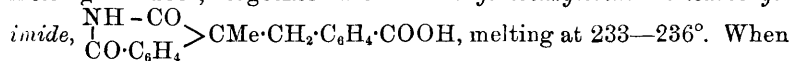
melting at 145°, together with *α-methyldibenzylortho-α-tricarboxyl-imide*, $\begin{matrix} NH-CO \\ | \\ CO \cdot C_6H_4 \end{matrix} > CMe \cdot CH_2 \cdot C_6H_4 \cdot COOH$, melting at 233—236°. When the former of these compounds is cohobated with hydriodic acid of 1·70 sp. gr., *α-methyldibenzylortho-α-tricarboxylmethylimide*,

$$\begin{matrix} NMe \cdot CO \\ | \\ CO \cdot C_6H_4 \end{matrix} > CMe \cdot CH_2 \cdot C_6H_4 \cdot COOH,$$
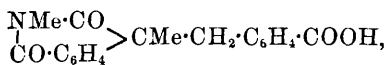
melting at 145—147°, is obtained. The synthesis of the last-named compound was attempted as follows:—α-Methylorthohomophthalic acid was evaporated to a syrup with an excess of aqueous methylamine, whereby α-dimethylhomophthalimide, $C_6H_4 < \begin{matrix} CHMe \cdot CO \\ | \\ CO --- NMe \end{matrix}$ (m. p. 64—66°), was obtained; this was converted by means of ortho-cyanobenzylic chloride into orthocyanobenzyl-α-dimethylhomophthalimide, $\begin{matrix} NMe \cdot CO \\ | \\ CO \cdot C_6H_4 \end{matrix} > CMe \cdot CH_2 \cdot C_6H_4 \cdot CN$, melting at 117—118°, and the

latter, when heated with hydrochloric acid at 220°, gave rise to *α-methyldibenzylortho-α-tricarboxylic acid,*

$$COOH \cdot C_6H_4 \cdot CH_2 \cdot CMe(COOH) \cdot C_6H_4 \cdot COOH,$$
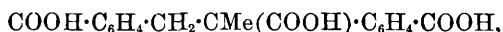
melting at 160°. The *anhydride* of the last-named acid,

$$COOH \cdot C_6H_4 \cdot CH_2 \cdot CMe {<}^{CO-O}_{C_6H_4 \cdot CO},$$
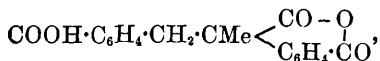
melts at 183—184°, and is formed by heating the acid at 180°.

When the yellow ammoniacal solution of dibenzyltricarboxyl-imide is exposed to the air, a colourless ammonium salt, $C_{17}H_{16}N_2O_5$, separates, melting at 197—198°. The corresponding *acid* crystallises with 1 mol. H_2O, and appears to be *α-oxydibenzylortho-α-tricarboxylaminelactonic acid,* $COOH \cdot C_6H_4 \cdot C(CONH_2){<}^{CH_2 \cdot C_6H_4}_{O-CO}$, or

$CONH_2 \cdot C_6H_4 \cdot C(COOH){<}^{CH_2 \cdot C_6H_4}_{O-CO}$; it melts and decomposes at 128—130°, and, if heated at 150—160°, it yields the *lactone* of α-hydroxydibenzyltricarboxylimide, $^{CO-O}_{C_6H_4 \cdot CH_2}{>}C{<}^{CO-NH}_{C_6H_4 \cdot CO}$, melting at 239—241°. When the lactonamic acid is boiled with alkali, ammonia is evolved, and the lactone of *α-hydroxydibenzyltricarboxylic acid,* $COOH \cdot C_6H_4 \cdot CH_2 \cdot C(COOH){<}^{C_6H_4}_{CO-}{>}O$, is formed; this melts and decomposes at 204—207°. In the hope of obtaining a salt of the corresponding acid, this lactone was boiled with barium hydroxide, and, after removing the excess of barium with carbonic anhydride, the filtrate was evaporated in a vacuum; the salt obtained had, however, the composition $C_{17}H_{10}O_6Ba + H_2O$, and was, therefore, a derivative of the lactone. If the lactone is heated at 220°, it yields J. Wislicenus' hydrodiphthalolactonic acid (*Ber.*, **17**, 2181), which is also probably identical with the lactone (m. p. 201°) obtained by Ephraim (*Abstr.*, 1891, 1493; compare also Hasselbach, *Annalen*, **243**, 253).

When the yellow solution of homophthalimide in potash is exposed to the air, the colour gradually disappears; no oxidation, however, takes place, homophthalamic acid being formed. If an alkaline solution of α-benzylhomophthalimide is exposed to the air it is oxidised, and *α-hydroxydibenzylorthodicarboxylic acid,*

$$CH_2Ph \cdot C(OH)(COOH) \cdot C_6H_4 \cdot COOH,$$

is produced; this melts at 130—133°, and gives α-benzylphthalide (m. p. 60—61°) when heated at 180°. When a solution of α-benzyl-phthalide in potash is evaporated and the residue heated at 212°, the isomeric *stilbeneorthocarboxylic acid,* $CHPh{:}CH \cdot C_6H_4 \cdot COOH$ (m. p. 158—160°), is formed.   A. R. L.

Action of Sodium on Monobromomesitylene. By P. Jannasch and M. Weiler (*Ber.*, **27**, 2521—2526).—The authors have obtained two isomeric *dimesityls*, $C_{18}H_{22}$, by heating bromomesitylene

with sodium in presence of benzene or ether. The compound comprising the minor portion of the product is a solid, crystallising in small plates having a feeble fluorescence resembling that of anthracene; it melts at 78—79°, and boils at 330° (corr.). Two *tetranitro*-derivatives were prepared from this solid hydrocarbon, the one melting at 205—206° and the other at 158—160°; a *tetrabromo*-derivative melting at 170—171°, and a *hexabromo*-derivative melting at 280°, were also prepared. The major portion of the product consists of a liquid *dimesityl* which boils at 312—320°, and has a bluish fluorescence; it yields a *tetranitro*-derivative melting at 233°, and a complex mixture of bromo-derivatives which have not as yet been separated.   A. R. L.

β-**Hydroxynaphthoic acid (m. p. 216°).** By H. GRADENWITZ (*Ber.*, **27**, 2621—2624; compare R. Hirsch, Abstr., 1893, i, 476; R. Möhlau, this vol., 138).—This acid is now known to be 2 : 3-hydroxynaphthoic acid (S. v. Kostanecki, this vol., i, 91). The author has reduced 2 : 3-chloronaphthoic acid with sodium amalgam, and obtained the dihydro-β-naphthoic acid which melts at 160°. The following derivatives of 2 : 3-hydroxynaphthoic acid are described for the first time.

1 : 2 : 3-*Bromhydroxynaphthoic acid*, $OH\cdot C_{10}H_5Br\cdot COOH$, is formed on brominating the acid in glacial acetic acid. It is deposited from acetic acid in long, yellow needles, and melts and decomposes at 233—235°; the *silver*, *lead*, and *barium* salts are not readily soluble.

The *monochlorinated acid* is obtained by the direct action of chlorine; it melts and decomposes at 231—233°. The mononitro-acid has been already described by S. Robertson (this vol., i, 137); its *methylic* salt, $NO_2\cdot C_{10}H_5(OH)\cdot COOMe$, is obtained by nitrating the methylic salt of β-hydroxynaphthoic acid. It separates from acetic anhydride in lustrous yellow plates, and melts at 189°. When reduced with tin and hydrochloric acid, it yields the *methylic* salt of amido-2 : 3-hydroxynaphthoic acid; this crystallises from methylic alcohol in yellow needles melting at 106°. From this substance by oxidation, *methylic* β-*naphthaquinonecarboxylate*, $C_{10}H_5O_2\cdot COOMe$, is obtained.

Methylic β-*naphthaquinolcarboxylate* [$OH : OH : COOMe = 1 : 2 : 3$] is formed when the methylic salt of amidohydroxynaphthoic acid is heated with dilute sulphuric acid. It crystallises from methylic alcohol in yellowish needles which melt at 99°.

The *acetyl*-derivative of 2 : 3-hydroxynaphthoic acid melts at 176—177°, and its *methylic* salt, $OAc\cdot C_{10}H_6\cdot COOMe$, crystallises in silky needles melting at 101°.   M. O. F.

Nitro-β-diazonaphthalenes. By F. GAESS and A. AMMELBURG (*Ber.*, **27**, 2211—2215).—3′-*Nitronaphthalene*-2 : 1-*diazoxide* is obtained by boiling 1 : 3′-dinitro-2-diazonaphthalene with absolute alcohol, nitrous acid being eliminated; the same result is attained by agitating the solution of the diazo-derivative with ice. It forms golden-yellow plates which explode at 142—145°. Heated with hydrochloric acid, it yields a *compound* which crystallises in yellow needles, and melts at 178°. The diazoxide is easily reduced with tin

and hydrochloric acid, the stannochloride of the resulting base separating in colourless needles. The *acetyl*-derivative melts at 261°.

1'-*Nitronaphthalene*-2 : 1-*diazoxide* is obtained in a similar manner to the foregoing compound. It explodes with great violence at 155—156°.

An aqueous solution of 1-nitro-2-diazonaphthalene spontaneously undergoes change, with formation of naphthalene-2 : 1-diazoxide (Bamberger, this vol., i, 295); at the same time, a black crystalline *compound* is formed, which explodes at 115°.   M. O. F.

Products of the Reduction of Alkylated Azo-colours of the Naphthalene Series. By O. N. WITT and H. v. HELMOLT (*Ber.*, **27**, 2351—2357).—Of the two bases obtained by the reduction of ethoxyanilineazo-α-naphthol, one has been already described (Abstr., 1892, 863). The remaining one forms a hydrochloride which dissolves readily in water, and crystallises in pale blue needles.

When ethoxyparatoluidineazo-α-naphthol is reduced, *ethoxyparatolylorthodiamidonaphthalene*,

$$OEt \cdot C_{10}H_5(NH_2) \cdot NH \cdot C_6H_4Me \quad [OEt : NH_2 : NH \cdot C_6H_4Me = 1:3:4],$$

is formed. It is deposited from petroleum in colourless needles, and melts at 118—119°. With benzile, it condenses to form *ethoxyparatolylnaphthostilbazonium chloride*, $OEt \cdot C_{10}H_5 \diagdown \begin{smallmatrix} NCl(C_6H_4Me) \cdot CPh \\ \parallel \\ N\text{———}CPh \end{smallmatrix}$,

which, when heated at 130° with alcoholic ammonia, yields a *substance* belonging to the saffranine group.

Ethoxyphenylnaphthotartrazonium chloride,

$$OEt \cdot C_{10}H_5 \diagdown \begin{smallmatrix} NPhCl \cdot C \cdot COOH \\ \parallel \\ N\text{———}C \cdot COOH \end{smallmatrix},$$
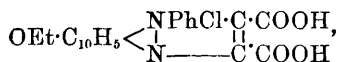
is obtained by warming ethoxydiamidophenylnaphthalene (*loc. cit.*) with sodium dihydroxytartrate in acetic acid solution on the water bath. The solutions in water and alcohol exhibit a brilliant green fluorescence, whilst the solution in strong sulphuric acid is dark red, becoming yellow on dilution. The homologue, *ethoxyparatolylnaphthotartrazonium chloride*, is obtained in an analogous manner; it forms hygroscopic, red needles, and hydrochloric acid causes a yellow *anhydride* to separate from the aqueous solution.

<div align="right">M. O. F.</div>

Products of the Reduction of Alkylated Azo-colours of the Naphthalene Series. By O. N. WITT and A. BUNTROCK (*Ber.*, **27**, 2358—2363).—*Phenetoilazo-α-ethoxynaphthalene*,

$$OEt \cdot C_6H_4 \cdot N{:}N \cdot C_{10}H_6 \cdot OEt,$$

is prepared by heating phenolazo-α-naphthol with ethylic bromide and alcoholic potash. It is deposited from alcohol and from benzene in yellowish-red needles and prisms having a blue reflex; the melting point is 122—123°. *Phenolazo-a-ethoxynaphthalene*, $OH \cdot C_6H_4 \cdot N{:}N \cdot C_{10}H_6 \cdot OEt$, is formed by uniting with phenol the azo-compound obtained by diazotising paramido-α-naphthol. It melts

at 171°. *Phenetoïlazo-α-naphthol*, $OEt \cdot C_6H_4 \cdot N:N \cdot C_{10}H_6 \cdot OH$, is formed when diazotised phenetidine combines with α-naphthol. It melts at 168°, dissolves in dilute potash, and forms a bluish-violet solution with strong sulphuric acid.

When reduced, phenetoïlazo-α-ethoxynaphthalene yields *ethoxyamidonaphthylphenetidine*, $OEt \cdot C_6H_4 \cdot NH \cdot C_{10}H_5(NH_2) \cdot OEt$, which forms snowy needles melting at 103° and becoming red when exposed to the air. It condenses with benzile to form *diethoxyphenylnaphthostilbazonium chloride*, $OEt \cdot C_{10}H_5 < \begin{matrix} NCl(C_6H_4 \cdot OEt) \cdot CPh \\ | \quad\quad\quad\quad || \\ N ———— CPh \end{matrix}$. The action of alcoholic ammonia on the latter converts it into the *saffranine*, $NH_2 \cdot C_{10}H_5 < \begin{matrix} NCl(C_6H_4 \cdot OEt) \cdot CPh \\ | \quad\quad\quad\quad || \\ N ———— CPh \end{matrix}$; this crystallises with $1H_2O$ in red needles, and melts at 150°. The *platinochloride* is red.

M. O. F.

Phenyl-β-naphthylaminesulphonic acids and Derived Azocolours. By R. LESSER (*Ber.*, **27**, 2363—2370).—When phenyl-β-naphthylamine is sulphonated, a mixture of phenyl-2-naphthylamine-4′-sulphonic acid and phenyl-2-naphthylamine-1′-sulphonic acid is formed (D.R.P. 53649). By the action of diazobenzenesulphonic acid on the former of these acids, a colouring matter is obtained which yields *phenonaphthazinesulphonic acid* when boiled with hydrochloric acid. This compound crystallises in lustrous, brown needles, and dissolves in water and alcohol, giving a red coloration with sulphuric acid. From the mode of formation, its constitution is

$$SO_3H \cdot C_{10}H_5 \overset{1}{\underset{2}{<}} \begin{matrix} N \\ | \\ N \end{matrix} > C_6H_4 \quad \text{(with } 4' \text{)}$$ (compare O. N. Witt, Abstr., 1887, 591).
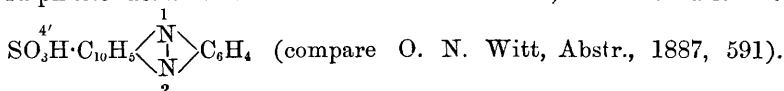
When fused with potash, the corresponding *eurhodole* is formed, the *potassium* salt of which is deposited from the melt in green crystals, dissolving in water to a red solution; from the latter, acetic acid liberates the free eurhodole in the form of a brown precipitate. The colouring matter obtained by the interaction of diazobenzenesulphonic acid and phenyl-2-naphthylamine-4′-sulphonic acid, has the constitution $\overset{2}{N}HPh \cdot C_{10}H_5(SO_3H) \cdot N_2 \cdot C_6H_4 \cdot SO_3H$ (with $4'$ and 1). On reduction with stannous chloride and hydrochloric acid, the corresponding phenylnaphthalenediaminesulphonic acid is formed.

The colouring matter obtained in an analogous manner from phenyl-2-naphthylamine-1′-sulphonic acid, crystallises from hot water in fine, orange-coloured needles; on adding hydrochloric acid, the free acid separates in the form of a bluish-violet precipitate. It yields an acid on reduction, which, however, does not unite with benzile or dihydroxytartaric acid, and fails to give the characteristic green coloration with ferric chloride. With α-naphthol in the presence of potassium ferricyanide, it gives rise to an indophenol, and as this reaction is peculiar to paradiamine-derivatives of the benzene series, it is clear that the azo-group, in the first instance, must have entered the benzene ring, taking up the paraposition to the naphthylamine residue. A comparison of the colour-

ing matter with the ammonium salt of phenylamidoazobenzene-sulphonic acid removes all doubt on this point.   M. O. F.

Naphthylbenzenesulphonamides and Naphthyltoluenesul-phonamides. By O. N. WITT and G. SCHMITT (*Ber.*, **27**, 2370—2377; compare Hinsberg, Abstr., 1891, 49).—These compounds are prepared by the action of benzenesulphonic or toluenesulphonic chloride on naphthylamine in the presence of caustic potash.

α-*Naphthylbenzenesulphonamide*, α-$C_{10}H_7\cdot NH\cdot SO_2\cdot C_6H_5$, forms white, silky needles and melts at 166—167°. Like all these substances, it dissolves readily in caustic alkali, less easily in ammonia and alkali carbonates. The β-*compound* melts at 102—103°. α-*Naphthyltoluene-parasulphonamide*, α-$C_{10}H_7\cdot NH\cdot SO_2\cdot C_7H_7$, is obtained in transparent prisms, which melt at 157°; the β-*compound* melts at 133°.

These four compounds react with azo-derivatives; α-naphthyl-tolueneparasulphonamide and diazobenzenechloride yielding an orange colouring matter, which crystallises from alcohol in needles, and melts at 201°. It is identical with the substance obtained by the action of tolueneparasulphonic chloride on anilineazo-α-naphthyl-amine. Reduction leads to the formation of paranaphthylene-diamine hydrochloride and tolueneparasulphonic chloride. Diazo-benzenesulphonic acid and diazotised naphthionic acid also form dyes with α-naphthyltolueneparasulphonamide, whilst from diazo-benzene chloride and β-naphthyltolueneparasulphonamide a red crystalline compound is obtained, which melts at 185°, and from diazobenzenesulphonic acid a substance crystallising in scarlet needles. Associated with the latter is a colourless substance, having the constitution $C_{10}H_6\underset{N}{\overset{N}{\big<}}{\big>}N\cdot C_6H_4\cdot SO_3K$, formed by the oxidation of the colouring matter; when this salt is heated in a closed tube with fuming hydrochloric acid at 210°, the parent substance, phenylazimidonaphthalene is obtained.   M. O. F.

Sulphonation in the Naphthalene Series. By O. DRESSEL and R. KOTHE (*Ber.*, **27**, 2137—2154).—In continuation of their in-vestigations of this subject (this vol., i, 378), the authors have examined the action of fuming sulphuric acid on 1 : 1'-naphthyl-aminesulphonic acid, and find that, in addition to sulphonation, the amido- and sulphonic-groups in the peri-position condense, with elimi-nation of water, the substances formed being sulphonic acids of the compound $C_{10}H_6\underset{SO_2}{\overset{NH}{\big<}}$, which the authors term *naphthosultam*, corre-sponding to the similar anhydride of 1 : 1'-amidonaphthol, to which Erdmann has given the name naphthosultone.

1 : 1'-*Naphthosultam*-2 : 4-*disulphonic acid*, $\underset{NH}{\overset{SO_2}{\big>}}C_{10}H_4(SO_3H)_2$, is obtained by heating the acid sodium salt of 1-naphthylamine-4 : 1'-disulphonic acid with fuming sulphuric acid at 80—90° for 5—6 hours. It is isolated in the usual manner as the *sodium* salt, $C_{10}H_4NS_3O_8Na_3 + 8\frac{1}{2}H_2O$, which crystallises in large yellow plates,

and is extremely stable, undergoing no change when heated at 180°; it is totally unacted-on by nitrous acid, and dissolves readily in water, giving solutions showing a fluorescence similar to that of fluoresceïn. On adding hydrochloric acid, it yields the *disodium* salt, which crystallises in slender, colourless needles, the solution of which rapidly decomposes carbonates with evolution of carbonic anhydride. All attempts to convert the acid into the corresponding naphthyl-aminetrisulphonic acid have been unsuccessful, the naphthosultam ring being extremely stable.

When the above sodium salt is fused with soda at 180—190°, it is converted into the *sodium* salt of 1-*amido*-1'-*naphthol*-2 : 4-*disulphonic acid*, $SO_3H \cdot C_{10}H_4(OH)(NH_2) \cdot SO_4Na + H_2O$, which crystallises in slender, colourless needles; its alkaline solution shows a green fluorescence. By the action of soda at 270°, the amido-group is also displaced by hydroxyl, with formation of 1 : 1'-*dihydroxynaphthalenedisulphonic acid*, whose *basic sodium salt*, $ONa \cdot C_{10}H_4(OH)(SO_3Na)_2 + 4H_2O$, crystallises in oblique prisms or plates having a greenish fluorescence. When heated with 20 per cent. fuming sulphuric acid at 160°, it is converted into 1 : 1'-dihydroxynaphthalene, proving that the above amidonaphtholdisulphonic acid is derived from 1 : 1'-amido-naphthol. That the sulphonic groups occupy the 2 : 4 positions is shown by the fact that the naphtholtrisulphonic acid obtained from naphthosultone (which, as will be proved later, is 1-naphthol-2 : 4 : 1'-trisulphonic acid) yields the same dihydroxynaphthalenedisulphonic acid on fusion with soda.

1-*Naphthol*-2 : 4 : 1'-*trisulphonic acid* is obtained by the action of fuming sulphuric acid on naphthosultone or on 1-naphthol-4 : 1'-disulphonic acid, and is isolated in the usual manner as the *sodium* salt, $OH \cdot C_{10}H_4(SO_3Na)_3 + 1\frac{1}{2}H_2O$; this is a white, sandy, crystalline powder, which is coloured deep blue by ferric chloride in aqueous solution; its alkaline solutions show a deep green fluorescence. It is incapable of yielding azo-colours, which renders it probable that the third sulphonic group occupies the 2-position; this is shown conclusively by the fact that on treatment with sulphuric and nitric acid two of the sulphonic groups are displaced by nitro-groups, with formation of the colouring matter "brilliant yellow," which is 1-naphthol-2 : 4'-nitro-1'-sulphonic acid.

1 : 1'-*Naphthosultamtrisulphonic acid*, $\begin{smallmatrix} SO_2 \\ | \\ NH \end{smallmatrix} > C_{10}H_3(SO_3H)_3$, is obtained by treating 1-naphthylamine-3 : 3' : 1'-trisulphonic acid with fuming sulphuric acid at 70—80°; its *trisodium* salt, with $4H_2O$, crystallises in stellate groups of white, microscopic needles, and does not yield fluorescent solutions. The *tetrasodium* salt, with $4H_2O$, is an indistinctly crystalline, yellow mass, and the *barium* salt a yellow, crystalline powder. The formation of this acid shows that Armstrong and Wynne's sulphonation rule does not hold invariably, not only in the β-, but also in the α-series.

The additional sulphonic group probably occupies the 4-position, but this has not been proved with certainty : it is very readily eliminated by the action both of acids and of alkalis, with formation of 1-1'-

naphthosultam-3 : 3'-*disulphonic acid*, the *trisodium* salt of which, with $4H_2O$, crystallises in deep yellow, microscopic, rhombic plates, whilst the *disodium* salt forms spherical aggregates of colourless, microscopic needles.   By fusion with soda, these salts are converted into 1 : 1'-amidonaphthol-3 : 3'-sulphonic acid   (D.R.P. 69,722 and 67,062).   Its acid *sodium* salt crystallises with $1\frac{1}{2}H_2O$ in asbestos-like aggregates of needles, the dilute solutions of which have a bluish-red fluorescence, which changes to reddish-violet on addition of alkalis.

When 2-naphthylamine-3' : 1'-disulphonic acid is heated with fuming sulphuric acid, a compound is obtained which no longer reacts with nitrous acid.   No anhydro-ring similar to that of the naphthosultam derivatives is formed in this case, but the amido-group itself is sulphonated, the new compound being 3' : 1'-*disulpho-naphthyl*-2-*sulphaminic acid*, $SO_3H\cdot NH\cdot C_{10}H_5(SO_3H)_2$; its *barium* salt crystallises with $10H_2O$ in orange-yellow needles, the *potassium* salt with $1H_2O$ in lustrous, orange-red needles, which on heating change to white, owing to the formation of sulphuric acid and the 3' : 1'-disulphonic acid.   The same reaction readily takes place in solutions of the salts, especially in presence of acids.   On further heating with fuming sulphuric acid, it undergoes a somewhat remarkable change, the sulphonic group migrating from the amido-group to the 1'-carbon atom, with formation of 2-naphthylamine-3 : 3' : 1'-trisulphonic acid (D.R.P. 27,378), the *acid potassium salt* of which crystallises with $1\frac{1}{2}H_2O$ in lustrous, white needles.   H. G. C.

Anthraquinoneoxime.   By E. SCHUNCK and L. MARCHLEWSKI (*Ber.*, **27**, 2125—2127).—Anthraquinoneoxime, $CO{<}^{C_6H_4}_{C_6H_4}{>}C{:}N\cdot OH$, is readily obtained by Goldschmidt's method (Abstr., 1884, 62), namely, heating anthraquinone with alcohol and hydroxylamine hydrochloride at 180°, and can be separated from the unaltered quinone by treating with alkalis, filtering, and reprecipitating the oxime with acid.   It crystallises from dilute alcohol in pale yellow, matted, slender needles, commences to sublime at about 200°, and melts, when quickly heated, at 224°.   It dissolves in alkalis, forming a reddish-brown solution, which is reprecipitated by carbonic anhydride; it is very stable towards hot concentrated sulphuric acid and towards Beckmann's mixture.   It is not acted on by acetic chloride, but readily yields alkyl-derivatives, the *methyl*- and *ethyl*-derivatives crystallising in pale yellow, matted needles, and the *benzyl*-derivative in golden-yellow needles; these are all decomposed by hydriodic acid, and therefore contain the alkyl-group in combination with the oxygen.

The determination of the molecular weight in Beckmann's apparatus gave results agreeing with the above formula.   H. G. C.

Oxidation of Cyclic Compounds.   By G. WAGNER (*Ber.*, **27**, 2270—2276; compare this vol., i, 469).—The author has oxidised French turpentine under the conditions previously described for menthene.   The product is separated into two fractions boiling, under

14 mm pressure, at 122—124° and 145—147° respectively; both these fractions are, however, mixtures. The fraction of higher boiling point gives analytical results agreeing with those required for pinene glycol, $C_{10}H_{18}O_2$. With carbanil, it yields a compound containing nitrogen, and when dehydrated by boiling with a few drops of hydrochloric acid, is converted into an oil which distils at 180—220°. The chief portion, however, distils at 18C—190°, and when treated with bromine yields pinol bromide, melting at 92—93°; the higher fractions yield a small quantity of a crystalline oxime. Besides these dehydration products, a third is obtained which is not volatile with steam, crystallises in quadratic tablets, melts at 191—191·5°, and has the composition $C_{10}H_{18}O_2$, and is probably an α-glycolen. From the fraction boiling at 145—147°, the author has separated a compound melting at 76—78°, probably the pure glycol. This does not react with hydroxylamine or ammoniacal silver solution, although the fraction boiling at 145—147° does.

The fraction of lower boiling point (122—124°), $C_{10}H_{16}O_2$, has the composition of a ketoalcohol; it does not, however, react with carbanil. After remaining some time, it deposits crystals which melt at 97°, and yield a crystalline oxime, $C_{10}H_{16}(NOH)_2$, melting at 130°.

E. C. R.

Terpene-like Hydrocarbons in Petroleum. By R. ZALOZIECKI (Ber., **27**, 2081—2087).

—A liquor was investigated that had been obtained in the purification of a mixture of crude petroleums from Potok and Wietirno. It was distilled with steam, then extracted with ether, and again distilled with superheated steam; the products were united and subjected to repeated fractionation, and the fractions, boiling respectively at 160—170° and 170—180°, were selected for further treatment. They were fractionated until they yielded products boiling respectively at 160—165° and 175—180°, and these were then treated separately with concentrated sulphuric acid. In this way, an oil (1) was obtained, partly polymerised but otherwise unaltered, and approximately of the composition C_nH_{2n-4}; when treated with bromine, it yielded a tetrabromodihydrocumene melting at 186° (uncorr.) in the first case, and a tetrabromodihydrocymene, melting at 205°, in the second. On adding water to the sulphuric acid solution, an oil (2) separated out containing oxygen, and apparently a hydroxyl-derivative. Dissolved in the water there remained a sulphonic acid; the barium salt of this, when hydrolysed with hydrochloric acid, yielded (3) an oil, which, when nitrated, formed in the first case, trinitroparaethyltoluene melting at 92°, and in the second a trinitrocymene melting at 126° (uncorr).

C. F. B.

Linalolene. By F. W. SEMMLER (Ber., **27**, 2520—2521).

—Linalolene, $C_{10}H_{18}$, is obtained by reducing linaloöl with sodium and absolute alcohol, or better, by heating linaloöl with zinc dust in a sealed tube at 220—230°. It boils at 165—168°, has a sp. gr. at 20° of 0·7882, and a specific refractive power $n_D = 1·455$; from these values it follows that linalolene contains two doubly-linked carbon atoms, and therefore, like linaloöl, belongs to the olefine series of

2 *u* 2

compounds. This view receives further support from the fact that linalolene, like the hydrocarbons of the citral series, when heated on the water bath with concentrated sulphuric acid, undergoes isomeric transformation into a hydrocarbon (*cyclolinalolene*) boiling at 165—167°, having a specific gravity at 17° of 0·8112, and a specific refractive power $n_D = 1·4602$, and therefore containing but one doubly-linked carbon atom. A. R. L.

Action of Sulphuric acid on Camphene. By G. BOUCHARDAT and J. LAFONT (*Compt. rend.*, **119**, 85—87).—Concentrated sulphuric acid acts energetically on camphene, but the action is less violent than with terebenthenes and terpilenes, the development of heat is less, and the products are different.

When racemic camphene is mixed, drop by drop, with one-tenth its weight of monohydrated sulphuric acid, the vessel being cooled, a homogeneous, almost colourless liquid is formed, without any separation of brown resinous acid substances. The chief product is the ether of inactive camphene borneol, $C_{40}H_{34}O_2$. It forms long, channelled, rhombohedral prisms, which melt at 90—91°, and boil at 322° under normal pressure, without undergoing any notable decomposition. Bromine yields an unstable additive product, and phosphorus pentachloride is without action on solutions in light petroleum at the ordinary temperature. Hydrochloric acid saturated at 0° has no action on the compound at 100°, but at 150° converts it into camphene hydrochloride. Fuming nitric acid attacks it in the cold with formation of camphor, and an acetic acid solution of chromic anhydride likewise oxidises it to camphor. Acetic anhydride is almost without action, but at 200° a small quantity of camphene is formed.

The other products are borneolsulphonic acid, which, by hydrolysis, yields the borneol of inactive camphene, and a small quantity of polymerides of camphene, the most abundant being $C_{40}H_{32}$.

The same ether of the borneol is obtained in small quantity by treating the camphene with a mixture of glacial acetic acid and sulphuric acid, but in this case the principal product is the borneol acetate of camphene borneol. C. H. B.

Pine Tar. By A. RENARD (*Compt. rend.*, **119**, 165—166).—Pine tar of sp. gr. 1·054 was found to contain water, 3·5; hydrocarbons boiling below 300°, 12·0; hydrocarbons boiling between 300° and 360°, 45·0; phenols, 18·0; resin rich in retene, 21·5 = 100·00°. In order to isolate the terebenthene, the fraction boiling between 160° and 180° is boiled with sodium to remove oxygen compounds, and is then fractionated. The terebenthene boils at 171—174°; sp. gr. at 0° = 0·866; rotatory power, $[\alpha]_D = 19·1°$; refractive index, 1·4785; vapour density, 4·6. It absorbs oxygen more rapidly than ordinary terebenthene. With bromine, in presence of carbon bisulphide, it yields an unstable additive product, $C_{10}H_{16}Br_2$, and with bromine alone it yields a tetra-substitution derivative, $C_{10}H_{12}Br_4$, an oily liquid, which after some time partially crystallises. The dihydrochloride melts at 49·5°, and is obtained by the action of hydrogen chloride on the

terebenthene alone, or in ethereal solution. When the terebenthene is mixed with ordinary sulphuric acid, it yields a polymeride boiling above 300°, cymene, and a small quantity of cymene hexahydride, $C_{10}H_{20}$, which boils at about 170°, and is not attacked by bromine or fuming nitric acid at the ordinary temperature. C. H. B.

Constitution of Camphor. By J. BREDT (*Ber.*, **27**, 2092—2099). —It is known that when camphor is oxidised the product consists, to the extent of about two-thirds, of camphoric and camphoronic acids. The author has now shown that the remainder contains oxalic, dimethylmalonic, succinic, and trimethylsuccinic acids; the method adopted was to convert the mixture of acids into a mixture of their ethylic salts, and to fractionate this under diminished pressure. The formation of these acids is further evidence in favour of the author's formula for camphor (this vol., i, 141). In the rest of the paper he attempts to refute the objections of Aschan (this vol., i, 422), and assigns the formula $COOH \cdot CMe < \genfrac{}{}{0pt}{}{CH_2 \cdot CH_2}{-CMe_2-} > C \cdot COOH$ to iso-camphanic acid, the relation of which to various other acids obtained from camphor is discussed. C. F. B.

Relation between the Rotatory Power of Camphor and the Molecular Weights of certain Solvents. By MOREAU (*J. Pharm.*, [5], **30**, 14—19).—Tables showing the rotatory power of camphor dissolved in aromatic hydrocarbons, alcohols of the fatty series, acids of the fatty series, and alkyl salts of fatty acids, are given. The author draws the following conclusions from the figures. (1) The rotatory power of camphor in solution increases with the concentration of the solution. (2) The rotatory power suffers no alteration with the lapse of time. (3) Solutions in isomeric modifications of the same solvent show the same rotatory power. (4) In an homologous series of solvents, the influence of concentration on rotatory power is the same; the rotatory power increases with the molecular weight of the solvent proportionally to the increase in the molecular weight. (5) The results indicate that the solvents form true combinations with the camphor, and it is not improbable that such a combination is effected at the summit of a tetrahedron adjacent to the radicle, C_3H_7. A. G. B.

Tautomerism of Oxymethylene Compounds. By O. ASCHAN and J. W. BRÜHL (*Ber.*, **27**, 2398—2404).—*Formylbromocamphor,* $C_8H_{14} < \genfrac{}{}{0pt}{}{CBr \cdot CHO}{CO}$, is prepared by the direct bromination of oxymethylenecamphor; it crystallises in four-sided, white leaflets melting at 44°, and is not acted on by bromine. It dissolves in concentrated sodium hydrogen sulphite, and is not precipitated from the solution by acids; with phenylhydrazine, it yields a *substance* which contains no bromine, and crystallises in hemihedral monosymmetric crystals melting at 124—125°. Formylbromocamphor is converted into bromocamphor by potash.

Methoxymethylenecamphor on bromination yields a crystalline

additive *product*, $C_{12}H_{18}Br_2O_2$, which melts at 78°; it evolves methylic bromide and hydrogen bromide in a vacuum giving formylbromocamphor. A similar unstable additive *product* is obtained from ethoxymethylenecamphor; it spontaneously decomposes into ethylic bromide and formylbromocamphor.

The above bromo-derivatives seem to be tautomeric in constitution with oxymethylenecamphor. W. J. P.

Camphorpinacone. By E. BECKMANN (*Ber.*, **27**, 2348—2350; compare this vol., ii, 434).—This substance is formed as a bye-product in the conversion of camphor into borneol by the prolonged action of sodium in ethereal solution (*Ber.*, **22**, 912). The *chloride*, $C_{20}H_{31}Cl$, which melts at 75°, is obtained by the action of hydrochloric acid on the pinacone, and, like that substance, it is optically active, having $[\alpha]_D = +45$; it is also formed when acetic chloride or phosphorus oxychloride acts on the pinacone. Similarly, hydrobromic acid gives rise to the *bromide*, which melts at 103°. The *methylic ether*, $C_{31}H_{34}O$, is obtained by the action of methylic alcohol on these compounds; it melts at 98°, and has $[\alpha]_D = -80°$. The *ethylic ether*, $C_{22}H_{36}O$, melts at 58°, and the *propylic ether*, $C_{23}H_{38}O$, at 86°. The *acetate* melts at 74°. If the chloride or bromide is mixed with acetic acid and an alcohol in which sodium has been dissolved, the ether of the alcohol employed is produced. These ethers are isomeric with those already described, but are not identical. The *methylic ether* melts at 67°, and has $[\alpha]_D = -133°$. The *ethylic ether* melts at 58°, whilst the *acetate*, obtained by adding zinc dust to a mixture of the halogen compound with ether and glacial acetic acid, melts at 109°.

The halogen in the chloride and bromide may be displaced by hydroxyl on treatment with moist silver oxide; the same result is produced by caustic potash or boiling water in the presence of zinc dust. The *hydroxy*-derivative obtained in this way melts at 120°, and is converted into the original chloride by the action of acetic chloride or hydrochloric acid. When treated with cold glacial acetic acid, it yields the acetate, which melts at 109°, the modification of lower melting point being formed when boiling acid is used. Phenylic isocyanate gives rise to a *compound*, $C_{27}H_{36}O_2N$, which melts at 161°.

When hydrogen chloride is eliminated from the chloride by the action of sodium carbonate at 150°, a *hydrocarbon*, $C_{20}H_{30}$, is formed, melting at 56°. It is unsaturated, and yields the chloride, melting at 75°, when treated with hydrogen chloride; the *nitrosochloride* melts at 150°, and the *dibromide* at 157°, the hydrocarbon being regenerated when zinc dust acts on the dibromide dissolved in acetone. Moist silver oxide converts the dibromide into the corresponding *glycol*, which melts at 150°. A *hydrocarbon*, $C_{20}H_{32}$, melting at 98°, is the final product of the action of hydrogen iodide on the hydrocarbon, $C_{20}H_{30}$, and it is also formed in the same way from the pinacone or its methylic ether. This substance, when treated with bromine, yields the dibromide already described. M. O. F.

Oxidation of Camphoric acid. By L. BALBIANO (*Ber.*, **27**, 2133—2137).—The author has repeated his experiments (Abstr., 1893,

i, 174) on the oxidation of camphoric acid on a larger scale, and finds that the bibasic acid obtained has the composition $C_8H_{12}O_5$, and its *calcium* salt the formula $C_8H_{10}O_5Ca + 2H_2O$. The *dimethylic salt*, $C_8H_{10}O(COOMe)_2$, is a thick, colourless liquid, which boils at 164—165° (corr.), has a sp. gr. of 1·145 at 15°/15°, a pleasant, resinous odour, and biting taste. The acid contains the hydroxyl group, as it readily yields *acetyl*- and *benzoyl*-derivatives, both of which are colourless oils, boiling respectively at 165—166° under 22 mm. pressure, and at 200° under 20 mm. pressure.

When reduced by a mixture of hydriodic acid and red phosphorus, it yields a mixture of two acids, $C_8H_{12}O_4$ and $C_8H_{14}O_4$, which are separated by the difference in the solubilities of their calcium salts, that of the former being almost insoluble in boiling water, although soluble in cold water. The acid, $C_8H_{14}O_4$, crystallises from water at 80°, in hard, white, prismatic crystals melting at 88—89°; its composition is that of a dimethyladipic acid, but it is not identical with Zelinsky's $\alpha_1\alpha_2$-dimethyladipic acid. The acid, $C_8H_{12}O_4$, crystallises in flattened prisms melting at 163—164° (corr.), and in composition and melting point resembles Perkin's cis-hexahydroisophthalic acid (Trans., 1891, 798); it is not, however, identical with that compound, as it is not converted into an anhydride by boiling with acetic chloride. By the action of potassium permanganate, it is reconverted into the acid, $C_8H_{12}O_5$.   H. G. C.

Action of Alkalis on Bromocamphoric Anhydride. By O. Aschan (*Ber.*, **27**, 2112—2116).

—Attempts to obtain a bromo-derivative of isocamphoric acid (this vol., i, 538) have not led to the desired result, the product being chiefly bromocamphoric anhydride. In one case, a small quantity of a brominated acid was obtained, which crystallises in needles, and melts at 196°, but the quantity was insufficient for analysis. When treated with alkalis, it is converted into an oily, unsaturated acid, which closely resembles lauranolic acid (Abstr., 1885, 669). An acid, apparently identical with the latter, is also obtained, together with camphanic acid, by the action of alkalis on bromocamphoric anhydride, as already observed by Fittig and Woringer; the author finds that, under suitable conditions, the yield of the unsaturated acid may rise as high as 17 per cent. The acid unites very readily with bromine, but hydrogen bromide is quickly evolved, and the product, after treatment with soda and recrystallisation from acetic acid, crystallises in large, pointed needles melting at 183—184°. It behaves as a brominated lactone, and is immediately oxidised by potassium permanganate, with formation of an acid soluble in water and ether; these products are being further investigated. The formation of an unsaturated acid from bromocamphoric acid, with evolution of carbonic anhydride and hydrogen bromide, is analogous to the decomposition of the β-bromo-fatty acids, and it therefore appears probable that in bromocamphoric acid the bromine atom is in the β-position to one of the carboxyl groups; Fittig, on other grounds, has already shown that the same atom is probably in the γ-position to the other carboxyl group.   H. G. C.

Picein, a Glucoside from the Leaves of Pinus picea. By TANRET (*Compt. rend.*, **119**, 80—83).—The finely chopped leaves of *Pinus picea* are treated with boiling water containing 5 grams of sodium hydrogen carbonate per kilo. of leaves, boiled for a few minutes, and allowed to macerate for 24 hours. The liquid is then precipitated successively with basic lead acetate and ammoniacal lead acetate. The latter precipitate is decomposed by sulphuric acid, the liquid filtered, neutralised with magnesium oxide, and evaporated to a syrup, which, whilst still warm, is mixed with one-third its weight of magnesium sulphate, and extracted with ethylic acetate. The latter is distilled, and the residue after being purified by treatment with absolute alcohol, is finally crystallised from boiling absolute alcohol or from boiling water.

Picein, $C_{14}H_{18}O_7$, whether anhydrous or hydrated, crystallises in silky, prismatic needles, with a bitter taste, soluble in 50 parts of water at 15°, and in an equal weight of boiling water; it is only slightly soluble in cold absolute alcohol, much more so in boiling alcohol, and insoluble in ether or chloroform. It is lævogyrate, $[\alpha]_D = -84°$ in aqueous solution, and $-78°$ in alcoholic solution. Anhydrous picein melts at 194°; the hydrate contains $1H_2O$.

Under the influence of emulsin, picein reacts with 1 mol. H_2O, and yields glucose and piceol in molecular proportion; dilute acids induce the same change, and the piceol crystallises equally well in both cases. Picein dissolves in concentrated sulphuric acid, with production of only a very faint brownish tinge, a reaction which distinguishes it from coniferin. It is not precipitated either by tannin, or by basic lead acetate, but with ammoniacal lead acetate it yields a precipitate of the composition $C_{14}H_{14}PbO_7$. It is also precipitated by magnesium sulphate, but does not combine with it. Although very slightly soluble in cold water, it dissolves readily in presence of the amorphous glucosides which accompany it in the leaves, and which seem to be its natural solvent.

When heated with acetic anhydride in presence of a small quantity of zinc chloride, picein yields a crystallisable tetracetate,

$$C_{14}H_{14}O_3(OAc)_4,$$
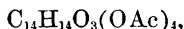
which melts at 170°, and is soluble in ether.

Piceol, $C_8H_8O_2$, melts at 109°, and dissolves in 100 parts of water at 15°, and in 14 parts of boiling water. With ferric chloride, it gives a violet coloration. It dissolves in solutions of alkali carbonates without liberation of carbonic anhydride, and with alkali hydroxides it forms crystallisable compounds, which are decomposed by carbonic anhydride, but not by water. It also forms an acetate and a benzoate, and generally behaves like a monhydric phenol. The barium compound has the composition $BaO(C_8H_8O_2)_2$, and the benzoate, which melts at 134, has the composition $C_8H_7O \cdot OBz$.   C. H. B.

Crystalline Form of Tetramethylbrazilin. By A. STENGEL (*Monatsh.*, **15**, 269—2,2; compare Schall, this vol, i, 257; Herzig, *ib.*, 341).—Tetramethylbrazilin crystallises in monosymmetric plates;

$a : b : c = 0.9392 : 1 : 0.9782.$ $\beta = 90° 23\frac{1}{2}'$. It is crystallographically very closely related to trimethylbrazilin. W. J. P.

γ-Amidovaleric acid and Methylpyrrolidone. By L. SENFTER and J. TAFEL (*Ber.*, **27**, 2313—2314).—*Benzoyl-γ-amidovaleric acid* forms white, interlacing crystals, melts at 132°, and when heated at higher temperatures loses the elements of water.

1-*Acetyl-2-methylpyrrolidone* is obtained by boiling methylpyrrolidone with acetic anhydride in a reflux apparatus. It is a pale yellow, limpid oil, boils at 224—226°, does not solidify at −17°, and has an odour resembling that of peppermint.

1 : 2-*Dimethylpyrrolidone* is obtained by heating methylpyrrolidone with methylic iodide for 12 hours, in a sealed tube, at 150°. It is a colourless oil, having a faint odour, boils at 215—217° under 743 mm. pressure, and does not solidify when cooled. E. C. R.

Action of Piperidine on Ethylic Acetoacetate. By F. B. AHRENS (*Ber.*, **27**, 2088—2089).—By mixing these two substances, and finally heating the mixture, acetopiperidine, $C_5NH_{10}Ac$, is obtained. It is a colourless oil, boils at 224°, or under 30—40 mm. pressure at 135—137°, and is decomposed by heating with acids or alkalis, or when its hydrochloride is heated, the products being piperidine and acetic acid. The hygroscopic *hydrochloride* melts at 95°, the deliquescent *hydrobromide* at 131—133, the red *platinochloride* at 107—109°, and the *aurochloride* at 67 −68°. C. F. B.

Action of Chloroform and Potash on Piperidine. By F. B. AHRENS (*Ber.*, **27**, 2090—2091)—When caustic potash is added to a mixture of chloroform and piperidine, and the whole finally warmed on the water bath, formylpiperidine, $C_5NH_{10}\cdot CHO$, is obtained. This has the properties ascribed to it by Wallach and Lehmann (*Annalen*, **237**, 252) and Lachowicz (*Monatsh.*, **9**, 700). C. F. B.

β-Bromoquinoline and γ-Bromoquinoline. By A. CLAUS and H. HOWITZ (*J. pr. Chem.*, [2], **50**, 232—239).—When kynurine is heated with phosphoric bromide, even with only a slight excess, and for a short time, and not above 120—130°, the hydroxyl is not simply replaced by bromine. The main product is colourless 3' : 4'-*dibromoquinoline*, melting at 82°, which, when heated at 200° with concentrated hydrochloric acid, yields colourless 3' : 4'-*dihydroxyquinoline*, melting at about 340°; some *monobromoquinoline* is, however, obtained. This melts at about 25°, and when heated to 270°, begins to boil, and is transformed into the above-mentioned dibromoderivative. It is readily soluble in cold dilute acids, is reconverted into kynurine when it is heated with hydrochloric acid at 150°, and cannot be converted into bromocarbostyril in the usual way. It readily unites with methylic iodide at 60—80°, forming a yellow compound that melts at 265−270°, and is not oxidised by alkaline ferricyanide to a crystalline quinoline. It has thus none of the properties of the monobromoquinoline obtained from quinoline by direct substitution; it can, however, be shown to be a 4'-derivative in the

following manner. Cinchoninic acid is known to be a 4'-carboxy-compound; when its ethylic salt is treated with concentrated aqueous ammonia at the ordinary temperature, colourless *cinchonin-amide*, melting at 181°, is formed. By carefully oxidising this with a slight deficiency of bromine in alkaline solution, 4'-*amidoquinoline*, melting at 69—70°, is obtained (together with some substance identical with the 3'-bromo-4'-amidoquinoline mentioned below). This 4'-amidoquinoline can be diazotised in sulphuric acid hydrate solution; when the product is poured into cuprous bromide solution, 4'-bromoquinoline is formed, identical with the bromoquinoline obtained from kynurine; if the product is poured into water, kynurine itself is produced.

If an attempt is made to diazotise 4'-amidoquinoline in hydrochloric acid solution, a chloroquinoline is formed, identical with that obtained by the action of phosphoric chloride on kynurine. If the attempt is made in hydrobromic acid solution, substitution takes place, and 3'-*bromo-4'-amidoquinoline* is formed. This melts at 203°, and sublimes unchanged. It can be diazotised in sulphuric acid hydrate solution, and, when the product is poured into alcohol, 3'-bromoquinoline is formed; this is found to be identical with the bromoquinoline obtained from quinoline by direct substitution.

The direct action of bromine on quinoline thus gives rise, not, as hitherto supposed, to 4'-, but to 3'-bromoquinoline.   C. F. B.

Synthesis of 3-Ethylisoquinoline. By F. DAMEROW (*Ber.*, **27**, 2232—2243; compare this vol., i, 279) —When orthocyano-benzylic cyanide is heated with propionic anhydride, it is converted into ψ-*dipropionylorthocyanobenzylic cyanide*,

$$CN \cdot C_6H_4 \cdot C(CN) {:} CEt \cdot O \cdot COEt,$$
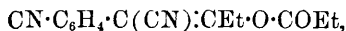
which crystallises in slender, silky needles, melting at 135·5°, together with a substance of higher melting point. The ψ-dipropionyl compound is converted by cold aqueous soda into 3 : 4-*ethyl-cyanisocarbostyril*, $C_6H_4{<}^{C(CN){:}CEt}_{CO --NH}$, which crystallises in light-brown, flat rhombic tablets melting at 261—262°. This substance is insoluble in aqueous acids, sparingly soluble in water, and insoluble in ammonia, but dissolves in boiling aqueous soda. It reacts with potash and methylic iodide to form 2 : 3 : 4-*methylethylcyanisocarbo-styril*, $C_6H_4{<}^{C(CN){:}CEt}_{CO --NMe}$, which crystallises in colourless needles, and melts at 135—136°. The corresponding ethylic derivative could not be obtained.

Ethylcyanisocarbostyril is converted by hot sulphuric acid into 3-*ethylisocarbostyril*, $C_6H_4{<}^{CH{:}CEt}_{CO \cdot NH}$, which crystallises from water in colourless, microscopic tablets melting at 140—141°. A better yield is obtained by the substitution of phosphoric acid for the sulphuric acid. Methylethylcyanisocarbostyril undergoes a similar change,

and is converted into 2 : 3-*methylethylisocarbostyril*, which forms splendid, colourless needles melting at 113—113·5°.

Ethylisocarbostyril is converted by phosphorus oxychloride into 1 : 3-*chlorethylisoquinoline*, $C_6H_4\!\!<\!\!\begin{array}{c}CH\!:\!CEt\\CCl\!:\!N\end{array}$, which forms colourless.

concentrically-arranged groups of needles, melts at 24°, and boils at 288° under a pressure of 751·5 mm.; it has faintly basic properties, but is precipitated from solution in hydrochloric acid by water. The *picrate* melts at 113—114°, the *platino hloride* forms small, flesh-coloured needles, which decompose at 290—300°, whilst the *aurochloride* melts at 160—161°.

3-*Ethylisoquinoline*, $C_8H_4\!\!<\!\!\begin{array}{c}CH\!:\!CEt\\CH\!:\!N\end{array}$, may be prepared by reducing chlorethylisoquinoline with hydriodic acid, or by distilling 3-ethyl-isocarbostyril with zinc dust. It is a colourless, very refractive liquid, boils at 255—256°, and has a strong odour of quinoline. The *picrate* forms yellow, rhombic tablets melting at 171—172°, the *platinochloride* melts and decomposes at 180°, and the *aurochloride* melts at 115—117°.

1 : 3-*Methoxyethylisoquinoline*, $C_6H_4\!\!<\!\!\begin{array}{c}CH\!:\!CEt\\C(OMe)\end{array}\!\!\gg\!\!N$, is obtained by the action of sodium methoxide on chlorethylisoquinoline. It is a colourless, very refractive, mobile liquid, boils at 266—267°, and has a pleasant odour. The *picrate* melts at 129°, whilst the *platinochloride* decomposes at 167°. *Ethoxyethylisoquinoline* boils at 274°; the *picrate* melts at 148°, and the *platinochloride* decomposes at 176°. *Phenoxyethylisoquinoline* is a brown oil. The *picrate* is a yellow, crystalline powder melting at 135—136°. When treated with bromine, this base forms an unstable *perbromide*, which gradually passes into 1-*bromophenoxy-3-ethylisoquinoline*; this crystallises from dilute alcohol in colourless needles melting at 58—59°.

The substance of higher melting point obtained in the preparation of dipropionylorthocyanobenzylic cyanide is also obtained in small amount when the latter is submitted to the action of alkalis. It forms yellow crystals melting and decomposing at 260—261°, and is a polymeride of orthocyanobenzylic cyanide, its molecular formula being $(C_9H_6N_2)_2$.

Ortho-α-dicyano-β-ethoxybutenylbenzene, $CN\cdot C_6H_4\cdot C(CN)\!:\!CEt\cdot OEt$, is obtained when dipropionylcyanobenzylic cyanide is acted on with alkali in the presence of alcohol. It forms colourless prisms, melts, after previously softening, at 58°, and is readily soluble in the usual solvents. Hydrochloric acid at 100° converts it into ethylic chloride and cyanethylisocarbostyril. When methylic alcohol is employed, the corresponding *methoxy*-derivative is obtained; this forms colourless, rhombic tablets, and melts at 66—67°.　　　　A. H.

Oxazolines and Thiazolines of the Anisic acid Series. By P. REHLÄNDER (*Ber.*, **27**, 2154—2161).—The bromalkylated anis-amides necessary for the preparation of the oxazolines and thiazolines of this series are obtained by treating anisic chloride with brom-

alkylamines and aqueous soda at a temperature not exceeding 30°. *β-Bromethylanisamide*, $OMe \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CH_2Br$, crystallises in colourless needles melting at 162°; *γ-bromopropylanisamide*,

$$OMe \cdot C_6H_4 \cdot CO \cdot NH \cdot [CH_2]_2 \cdot CH_2Br,$$

in needles melting at 77·5°; and *β-bromopropylanisamide*,

$$OMe \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CHMeBr,$$

in slender needles melting at 85°.

To prepare the oxazolines, the alkylanisamides are dissolved in warm alcohol and treated with the requisite quantity of alcoholic potash. *Mesoparamethoxyphenyloxazoline*, $OMe \cdot C_6H_4 \cdot C {\small\begin{smallmatrix}O\\N\end{smallmatrix}} > C_2H_4$, crystallises from light petroleum in colourless plates melting at 63°, the *picrate* melts at 192°, the *aurochloride*, $C_{10}H_{12}O_2N,AuCl_4$, at 164—166°. *Mesoparamethoxyphenylpentoxazoline*, $OMe \cdot C_6H_4 \cdot C {\small\begin{smallmatrix}O \cdot CH_2\\N \cdot CH_2\end{smallmatrix}} > CH_2$, is an oil, and yields a *hydrobromide*, which, after crystallisation from alcohol, melts at 143°; the *picrate* melts at 131—133°, and the *platinochloride* at 187—188° with decomposition. *β-Methylmesoparamethoxyphenyloxazoline*, $OMe \cdot C_6H_4 \cdot C {\small\begin{smallmatrix}O \cdot CHMe\\ |\\N \cdot CH_2\end{smallmatrix}}$, is also an oil; the *hydrobromide* melts at 179°, the *picrate* at 177°, and the *platinochloride* at 201°.

The bromalkylanisamides are also converted by boiling with water into the hydrobromides of the oxazolines, but these again take up water, yielding *amidoalkylic anisates*, thus—

$$OMe \cdot C_6H_4 \cdot C {\small\begin{smallmatrix}O \cdot CH_2\\ |\\N \cdot CH_2\end{smallmatrix}} + H_2O = OMe \cdot C_6H_4 \cdot COO \cdot C_2H_4 \cdot NH_2.$$
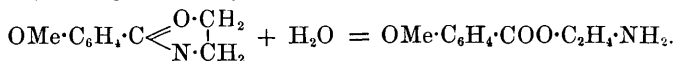
β-Amidoethylic anisate crystallises in colourless plates melting at 52°; the *hydrobromide* in needles melting at 199—200°; the *picrate* melts at 173°; and the *platinochloride* at 217°. The *hydrobromide* of *γ-amidopropylic anisate*, $OMe \cdot C_6H_4 \cdot COO \cdot [CH_2]_3 \cdot NH_2, HBr$, melts at 95—97°; the *picrate* at 161—162°; and the *platinochloride* at 205°. The *hydrobromide* of *β-amidopropylic anisate*,

$$OMe \cdot C_6H_4 \cdot COO \cdot CH_2 \cdot CHMe \cdot NH_2, HBr,$$

melts at 164—167°; the *picrate* at 189°; and the *platinochloride* at 213°.

The thioanisamide necessary for the preparation of the thiazolines was obtained by distilling anisic acid with lead thiocyanate, and treating the anisonitrile thus obtained with alcoholic ammonium sulphide at 100°. *Anisonitrile*, $OMe \cdot C_6H_4 \cdot CN$, boils at 245—255°, and crystallises at the ordinary temperature; and *thioanisamide*,
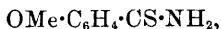
$$OMe \cdot C_6H_4 \cdot CS \cdot NH_2,$$

crystallises from hot water in yellow plates melting at 148—149°. When boiled with ethylenic bromide, it is converted into *mesoparamethoxyphenylthiazoline*, $OMe \cdot C_6H_4 \cdot C {\small\begin{smallmatrix}S \cdot CH_2\\ |\\N \cdot CH_2\end{smallmatrix}}$, which crystallises from

light petroleum in well-developed, yellowish crystals melting at 54·5°; its *picrate* melts at 187°; and its *platinochloride* at 213° with decomposition. *Mesoparamethoxyphenylpenthiazoline*,

$$OMe \cdot C_6H_4 \cdot C \ll^{S \cdot CH_2}_{N \cdot CH_2} > CH_2,$$
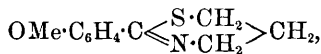
obtained by boiling thioanisamide with trimethylene chlorobromide, crystallises from light petroleum in well-developed, colourless crystals melting at 46°; its *picrate* melts at 107—108°; and its *platinochloride* at 204° with decomposition.   H. G. C.

Constitution of Söderbaum and Widman's Phenyldihydroketometadiazines and Phenyldihydrothiometadiazines. By C. PAAL and L. VANVOLXEM (*Ber.*, **27**, 2413—2427).—Busch (Abstr., 1892, 1495) obtained phenyltetrahydroketoquinazoline,

$$C_6H_4 <^{NH \cdot CO}_{CH_2 \cdot NH},$$
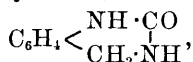
melting at 189°, by the action of carbonyl chloride on orthoamidobenzylaniline. Now Söderbaum and Widman (Abstr., 1890, 178) had given this formula, with the name " benzophendihydroketometadiazine," to the compound melting at 145—146°, obtained from orthoamidobenzylic alcohol and phenylcarbimide. This compound, however, is now shown to exhibit none of the reactions of Busch's ketoquinazoline; it must, therefore, have the alternative formula

$$C_6H_4 <^{NH \cdot C:NPh}_{CH_2 \cdot O},$$
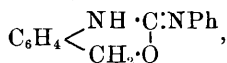
and the name phenylimidocoumazone is assigned to it.

Phenylimidocoumazone is a basic substance; the *hydrochloride* melts at 102°. It is reduced by sodium in alcoholic solution to aniline and orthotoluidine. With acetic and benzoic chlorides, it forms additive products melting at 119° and 117° respectively; and it also yields oily additive products with the corresponding acid anhydrides. When boiled with aniline, it yields Busch's phenyltetrahydroketoquinazoline, together with some symmetrical diphenylcarbamide; with paratoluidine, it reacts in an analogous manner. It behaves thus in an entirely different manner from phenyltetrahydroketoquinazoline.

In a similar way, it is shown that Söderbaum and Widman's benzophenyldihydrothiometadiazine, melting at 197° (obtained from orthoamidobenzylic alcohol and phenylthiocarbimide, Abstr., 1889, 973), does not behave like Busch's phenyltetrahydrothioquinazoline, $C_6H_4 <^{NH \cdot CS}_{CH_2 \cdot NPh}$, which was obtained from orthoamidobenzylaniline and carbon bisulphide in alcoholic potash solution, and melts at about 245°. To the former compound the formula $C_6H_4 <^{NH \cdot C:NPh}_{CH_2 \cdot S}$, and the name *phenylimidocoumothiazone*, are assigned. This compound has basic properties, is reduced by sodium in alcoholic solution
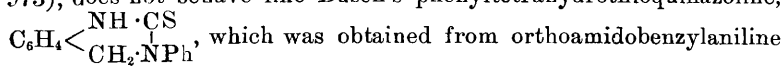
to aniline and orthotoluidine, yields additive compounds with acetic and benzoic chlorides (melting, in the latter case, at 140°), and does not react with aromatic amines.   C. F. B.

Synthesis of Coumothiazone Derivatives. By C. PAAL and O. COMMERELL (*Ber.*, **27**, 2427—2433).—When orthoamidobenzylic alcohol is boiled with carbon bisulphide in alcoholic potash solution, yellowish *thiocoumothiazone*, $C_6H_4 <^{NH \cdot CS}_{CH_2 \cdot S}$ or $C_6H_4 <^{N = C \cdot SH}_{CH_2 \cdot S}$, melting at 166°, is formed. It has acid properties, forming crystallised *potassium* and *sodium salts*, and, when boiled with methylic iodide in alcoholic potash solution, it yields a yellowish, *methyl*-derivative melting at 73°. In boiling alcoholic solution, it is reduced by sodium to orthotoluidine. When boiled with aniline, it yields *phenylimidocoumothiazone*, $C_6H_4 <^{NH \cdot C:NPh}_{CH_2 \cdot S}$, and some *phenyl-tetrahydrothioquinazoline*, $C_6H_4 <^{NH \cdot CS}_{CH_2 \cdot NPh}$ (compare preceding abstract). With paratoluidine, it acts in an analogous fashion, yielding *paratolylimidocoumothiazone*, melting at 187°, and *paratolyl-tetrahydrothioquinazoline*.   C. F. B.

Pyrazolone and Isopyrazolone. By R. v. ROTHENBURG (*J. pr. Chem.*, [2], **50**, 227—231).—The author denies that Ruhemann can have isolated isopyrazolone (this vol., i, 476): the substance obtained by the latter must have been a polymeride of pyrazolone. Pyrazolone and isopyrazolone are, he reasserts, tautomeric, and isomeric only in their derivatives. In proof of this he states that 3-phenyl-pyrazolone acts both as a pyrazolone- and as an isopyrazolone-derivative. As a pyrazolone derivative $^{N=CPh}_{NH \cdot CO}>CH_2$, in that it yields with benzaldehyde a reddish-brown 4-*benzal-derivative*,

$$^{N=CPh}_{NH \cdot CO}>C:CHPh,$$
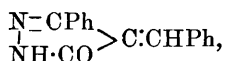
not melting below 250°; and with nitrous acid a red 4-*isonitroso-derivative*, melting at 184°, the purple-red silver salt of which explodes at 242°. As an isopyrazolone derivative, $^{NH \cdot CPh}_{NH—CO}>CH$, in that it yields with excess of acetic anhydride a 1 : 2-*diacetyl derivative*, $^{NAc \cdot CPh}_{NAc—CO}>CH$, melting at 86°, and its 4-azobenzene derivative yields with benzaldehyde a red compound $CHPh<^{N \cdot CPh}_{N—CO}>CH$, melting at 131°. Further, 3 : 4-dimethylpyrazolone yields, with acetic anhydride, 1 : 2-*diacetyl-3 : 4-dimethylisopyrazolone*, melting at 44°; whilst 3 : 4 : 4-trimethylpyrazolone, in which the movable hydrogen that is the cause of the tautomerism is replaced by methyl, yields only a 1-*acetyl-3 : 4 : 4-trimethylpyrazolone*.   C. F. B.

Phenylisoxazoloneimide. By R. v. ROTHENBURG *(J. pr. Chem.,* **50**, 231).—A question of priority. The author admits that Burns (Abstr., 1893, i, 315) had, before himself, assigned the right constitution to phenylisoxazoloneimide, and apologises for having overlooked his work. C. F. B.

The Aldehydine Reaction. By O. HINSBERG and F. FUNCKE *(Ber.,* **27**, 2187—2193).—Phenyleneamidines (the aldehydines of Ladenburg) have already been shown to result from the action of aldehydes on orthodiamines (Abstr., 1887, 817).

Acetaldehydine, $C_6H_4 < ^{NEt}_{—N} > CMe$, is obtained from acetaldehyde and orthophenylenediamine, or by heating ethylorthophenylenediamine with glacial acetic acid at 170°; it is a colourless oil, which boils at 257° (60 mm.), and becomes red in the air (compare Hempel, Abstr., 1890, 612). The *hydriodide,* $C_{10}H_{12}N_2, HI + H_2O$, loses water at 110°, and melts at 159·5—160°; the *nitrate* is anhydrous. *Ethenylphenyleneamidine,* $C_6H_4 < ^{—N}_{NH} > CMe$, which is formed in association with the foregoing base, may be separated from it by its insolubility in ether, when impure; it melts at 175°, and in the pure state dissolves readily in ether.

Propylaldehydine, $C_6H_4 < ^{NPr^a}_{—N} > CEt$, from propaldehyde, is a yellow oil of bitter taste; the *hydriodide,* $C_{12}H_{16}N_2, HI + H_2O$, becomes anhydrous at 100°, and melts at 128—129°. *Propenylphenyleneamidine,* $C_6H_4 < ^{—N}_{NH} > CEt$, is separated similarly to the lower homologue; it melts at 177—178°.

Paranitrobenzylideneorthophenylenediamine,

$$NH_2 \cdot C_6H_4 \cdot N:CH \cdot C_6H_4 \cdot NO_2,$$

is prepared by mixing alcoholic solutions of paranitrobenzaldehyde and orthophenylenediamine in molecular proportion. It forms red plates of metallic lustre; partial fusion takes place at 134°, becoming complete at 180°. When excess of the aldehyde is employed, *dinitrobenzylideneorthophenylenediamine,* $C_6H_4(N:CH \cdot C_6H_4 \cdot NO_2)_2$, is formed; this crystallises from chloroform in bright yellow needles which melt at 222°; similarly to the foregoing substance, regeneration of orthophenylenediamine is effected by heating with hydrochloric acid.

Paranitrobenzenylphenyleneamidine, $C_6H_4 < ^{—N}_{NH} > C \cdot C_6H_4 \cdot NO_2$, can be prepared by boiling the alcoholic solution of nitrobenzlidenephenylenediamine for 10 hours; it separates from nitrobenzene in hexagonal prisms which melt at 322°. The *acetate* of the anhydrobase is also formed from the mononitro- and dinitro-derivatives by warming with glacial acetic acid. It is obtained in the form of yellow needles which melt at 300°. In the latter reaction, *dinitrobenzaldehydine,* $C_6H_4 < ^{——N}_{N(CH_2 \cdot C_6H_4 \cdot NO_2)} > C \cdot C_6H_4 \cdot NO_2$, is also formed; it melts at 212·5°. M. O. F.

Hydrogenised Quinoxalines. By O. HINSBERG and F. KÖNIG (*Ber.*, **27**, 2181—2187).—Dihydrodiphenylquinoxaline is obtained by reducing diphenylquinoxaline with stannous chloride (compare O. Fischer, Abstr., 1891, 747); it forms dark yellow prisms which melt at 146°. The *stannochloride* crystallises in shining plates, bluish-black in colour. The *nitroso*-derivative forms pale yellow needles which melt at 138°.

Complete reduction of diphenylquinoxaline by means of sodium and alcohol leads to the formation of two tetrahydro-derivatives in nearly equal quantities, the isomerism which they exhibit being stereochemical in character; all attempts, however, to convert one modification into the other have hitherto been unsuccessful. *α-Tetra-hydrodiphenylquinoxaline*, $C_6H_4{<}^{NH\cdot CHPh}_{NH\cdot CHPh}$, crystallises from alcohol in colourless leaves which melt at 106°. It is readily oxidised by nitric acid and by silver nitrate, the latter producing in an alcoholic solution of the base a green coloration, which accompanies the formation of a mirror; when warmed with sulphuric acid, it develops a red tint. The *hydrochloride* melts at 225°; the *diacetyl*-derivative crystallises in needles which melt at 170°. *β-Tetrahydrodiphenylquinoxaline* melts at 142·5°: it is much less soluble in alcohol than the α-modification, and the reduction of silver nitrate is accompanied by a red coloration. The *hydrochloride* melts at 228°, and the *diacetyl*-derivative forms colourless prisms which melt at 192·5°.

Quinoxalinedicarboxylic acid, $C_6H_4{<}^{N{:}C\cdot COOH}_{N{:}C\cdot COOH} + 2H_2O$, is obtained in the form of its sodium salt by the interaction of sodium dioxytartrate and orthophenylenediamine. The acid forms colourless prisms which lose water at 110°, and melt at about 190° with elimination of carbonic anhydride. On reduction with hydriodic acid, a bluish-black *compound* is formed, probably of the composition $C_{40}H_{26}N_8O_{16}$; it is acid in character, and decomposes at 170°.

M. O. F.

Oxidation of Tolualloxazine. By O. KÜHLING (*Ber.*, **27**, 2116—2119).—When tolualloxazine (Abstr., 1891, 1341; 1892, 70) is oxidised by means of alkaline potassium permanganate, it is converted into oxalic acid and a relatively small quantity of a new acid, which is readily separated from the former, as it forms a soluble calcium salt. To isolate the acid, the calcium salt is converted into the barium salt, and the latter decomposed by the requisite quantity of sulphuric acid. It crystallises from boiling water in slender, lustrous prisms, containing water of crystallisation, which is partly evolved on exposure to the air. It melts and decomposes at 265°, and, after drying at 110°, has the composition $C_8H_6N_4O_7$. It has probably one of the following constitutional formulæ.

$$\begin{array}{l} COOH\cdot C{:}N{:}C\cdot NH\cdot CO \\ COOH\cdot C{:}N{:}C\cdot CO\cdot NH \end{array} + H_2O \text{ or } \begin{array}{l} COOH\cdot C{:}N{:}C\cdot NH\cdot CO \\ COOH\cdot C{:}N{:}C\cdot CO\cdot O{-} \end{array}{>}NH_3.$$
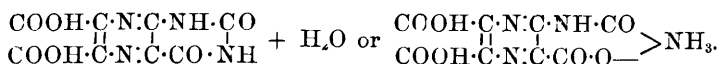
The author regards the second of these formulæ, according to which it is a betaïne-like condensation product of the acid,

$$COOH \cdot \overset{|}{C} \cdot N \colon \overset{|}{C} \cdot NH \cdot CO \cdot NH_2$$
$$COOH \cdot C \cdot N \colon C \cdot COOH$$,
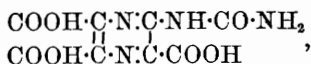
as the more probable, and the examination of the metallic and alkylic salts, although not yet concluded, points to the same conclusion. The *barium* salt, $C_8H_4N_4O_7Ba$, forms yellowish-white, microcrystalline needles, and the *silver* salt a yellow, amorphous precipitate.

<div align="right">H. G. C.</div>

New Reaction between Carbon Bisulphide and Primary Hydrazines. By M. Busch (*Ber.*, **27**, 2507—2520).—When carbon bisulphide is added to an alcoholic solution of phenylhydrazine, phenylhydrazine phenylsulphocarbazinate separates, and, if this is treated with alcoholic potash at a moderate temperature, it passes into solution; the filtrate deposits long, almost colourless needles of the *potassium* derivative of *phenyldithiobiazolone hydrosulphide*, $C_8H_5N_2S_3K$, which melts at about 240°. *Phenyldithiobiazolone hydrosulphide*, $\overset{NPh \cdot N}{\underset{CS-S}{|}} \!\!> SH$, is obtained on adding hydrochloric acid to a solution of the potassium salt. It crystallises in small, white needles, melts at 90—91°, boils and partly decomposes at about 230°, and becomes yellow on exposure to the air, owing to the formation of bisulphide (see below). Its acidic properties are strongly pronounced, and its salts are not decomposed by acetic acid; it is unstable towards reducing agents. The acetyl derivative, $C_8H_5N_2S_4Ac$, melts at 121—122°, and the *methylic* salt at 108—109°. The *bisulphide*, $(C_8H_5N_2S_2)_2S_2$, is best prepared by adding ferric chloride to an alcoholic solution of the hydrosulphide or its potassium salt; it crystallises in intensely yellow needles, melts at 124—125°, and, when boiled with alcoholic potash, yields the potassium salt of the hydrosulphide, together with the sulphinate $C_8H_5N_2S_2 \cdot SO_2K$.

Phenyldithiobiazolonesulphonic acid, $C_8H_5N_2S_2 \cdot SO_3H$, is obtained as potassium salt by treating an aqueous solution of the potassium salt of phenyldithiobiazolone hydrosulphide with potassium permanganate, and evaporating the filtrate; the salt, so obtained, forms yellow needles, and melts at 268°.

Phenylthiobiazolone hydrosulphide, $\overset{NPh \cdot N}{\underset{CO-S}{|}} \!\!> SH$, is prepared by adding carbon bisulphide to phenylhydrazine dissolved in alcohol, and treating the resulting paste with alcoholic potash, whereby potassium phenylsulphocarbazinate is obtained; this is then suspended in benzene and treated with carbon oxychloride. The hydrosulphide forms stout needles, and melts at 86—87°; the *bisulphide*, $(C_8H_5N_2OS)_2S_2$, melts at 78—79°.

Phenylpentahydro-1 : 3 : 5-*diazthine*, $NPh \!\!<\!\! \overset{CH_2 \cdot CH_2}{\underset{NH-CS}{}} \!\!> S$, is obtained by heating potassium phenylsulphocarbazinate with ethylene dibromide; it forms tufts of needles, and melts at 94°. The *hydrochloride*,

$C_9H_{10}N_2S_2.HCl$, melts and decomposes at 188°, and the *acetyl*-derivative, $C_9H_9N_2S_2Ac$, is an oil.

Thiobiazolone hydrosulphide, $\begin{smallmatrix} N\cdot N \\ | \quad \\ SH\cdot C\cdot S \end{smallmatrix}\!\!>\!\!C\cdot SH$, is obtained by adding a mixture of carbon bisulphide and alcohol to an aqueous solution of hydrazine sulphate, and boiling the mixture with alcoholic potash; the *hydrazine* salt, $C_2H_2N_2S_3,N_2H_4$, so obtained, melts at 185°. The *hydrosulphide* is prepared by decomposing the latter salt with hydrochloric acid; it forms stout, yellow crystals, and melts at 168°. The *potassium* salt melts at 285° with decomposition; the *monobenzoyl*-derivative melts at about 220°, the *dibenzoyl*-derivative at 184—185°, and the *dibenzylic*-derivative, $C_2N_2S_3(CH_2Ph)_2$, at 89°.

<div align="right">A. R. L.</div>

Hydronaphthinolines. By A. REISSERT (*Ber.*, **27**, 2244—2260; compare this vol., i, 385).—The name naphthinoline is given to a base of the following formula, the various substitution products being distinguished by means of the symbol shown.
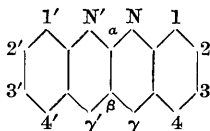
Diorthonitrodibenzylacetic acid, $(NO_2\cdot C_6H_4\cdot CH_2)_2CH\cdot COOH$, is obtained by heating ethylic diorthonitrobenzylmalonate with hydrochloric acid of sp. gr. 1·19 at 190°. It crystallises from dilute alcohol in delicate, almost white needles, melting at 149°, and is very sparingly soluble in water, readily in alcohol, &c. The *ammonium* salt, $C_{16}H_{14}N_2O_6,NH_3 + \frac{1}{2}H_2O$, forms long, silky needles, and melts, after decomposing to some extent, at 120°. The *ethylic* salt crystallises in flat, white prisms, and melts at 62°.

Orthoparadinitrodibenzylacetic acid is also obtained when impure orthonitrobenzylic chloride is used. It forms microscopic, flat needles, melting at 131°.

Δ^N-*Tetrahydro-α-naphthinoline* $[H_4 = \beta : \gamma : \gamma' : N']$ is best obtained by reducing dinitrodibenzylacetic acid in alcoholic solution with hydrogen chloride and zinc dust. It forms colourless plates, with a silvery lustre, melts at 211—212°, and decomposes a few degrees above this temperature. It is readily soluble in alcohol, &c., very sparingly in water. The *hydrochloride* crystallises with $2H_2O$ in long, soft, light yellow needles, or, with $1H_2O$, in hard, pointed, light yellow, well-developed prisms. It is very sparingly soluble in aqueous hydrochloric acid; the anhydrous compound melts at about 270°. The *sulphate* is also yellow, and is very sparingly soluble in water, somewhat more readily in alcohol; it melts at 222°. The *picrate* forms yellow prisms, which melt and decompose at 208°. The *platinochloride* melts and decomposes violently at 271°, and the *aurochloride* at 192°. The *mercurochloride* forms lustrous, yellow needles and melts at 232—233°.

$\Delta^N N'$-*Methyltetrahydro-α-naphthinoline* $[Me = N']$ is obtained when

the base is treated with an excess of methylic iodide. It forms lustrous, almost white plates, melting at 114°. $\Delta^N N'$-*Acetyltetrahydro-α-naphthinoline*, $C_{16}H_{13}N_2Ac$, forms small needles, melting at 240°. It is soluble in warm aqueous acids.

Dibromotetrahydronaphthinoline, $C_{16}H_{12}Br_2N_2$, is formed by the action of bromine water on an aqueous solution of the hydrochloride of the base. It separates from acetic acid in brownish-yellow, compact needles, containing 3 mols. of acetic acid, which are lost at 100°, yellow crystals being left, which melt at 244°.

$\Delta^{N\gamma}$-*Dihydro-α-naphthinoline* [$H_2 = N' : \gamma$]. Oxidising agents convert the tetrahydro-compound into this substance, and it is also obtained when the tetrahydro-compound is distilled with zinc dust. It has not hitherto been found possible to prepare naphthinoline itself. The dihydro-derivative is best prepared by the use of mercuric acetate. The *hydrochloride* forms small, deep orange-yellow crystals, and melts at about 230°; it is less readily soluble in water and alcohol than the corresponding tetrahydro-derivative. The free base crystallises from alcohol in lustrous, almost white plates, melting at 201°. The solutions of the base and its salts show a strong, green fluorescence; the vapours from hot solutions of the base cause great irritation of the skin of the face. The *picrate* melts and decomposes at 241°, the *platinochloride* and *mercurichloride* do not melt below 300°, and the *aurochloride* forms deep red needles.

$\Delta^{N\gamma}N'$-*Acetyldihydro-α-naphthinoline*, $C_{16}H_{11}N_2Ac$, forms lustrous, white crystals, melting at 174°. The dihydro-compound, therefore, is a secondary base, and its stability towards oxidising agents is probably to be accounted for by the asymmetrical distribution of the hydrogen atoms.

Hexahydro-α-naphthinoline [$H_6 = α : β : N : N' : \gamma : \gamma'$] is obtained by the addition of sodium to a boiling alcoholic solution of the tetrahydro-base. It forms long, white needles, containing $\frac{1}{2}H_2O$, which melt at 128°. Both the free base and its salts readily oxidise in the air. The *picrate* is readily soluble in alcohol. A. H.

Conium Alkaloïds. By R. WOLFFENSTEIN (*Ber.*, **27**, 2611—2615). —The angle of rotation observed for a specimen of pure coniine being abnormally high ($+16.4°$ in a 0.992 decimetre tube at 19°), the base was purified by conversion into the hydrogen tartrate. On treating with potash the filtrate from the crystals of this salt, it yielded a mixture of bases, from which *d*-coniine was removed in the form of the nitroso-derivative; the residual base was *n*-methylconiine (compare Passon, Abstr., 1891, 1118). The observed angle of rotation for *n*-methylconiine in a 0.333 decimetre tube is $+22.6°$.

The author draws attention to some slight confusion which has crept into the literature of this subject. M. O. F.

Coniine. By R. WOLFFENSTEIN (*Ber.*, **27**, 2615—2621).—An exact description of various well-known *d*-coniine salts is given in this paper. The crystallographic examination of *d*-coniine platinochloride reveals the fact that a small quantity of the base was present in Ladenburg's isoconiine (Abstr., 1893, i, 442), the latter, therefore,

has a specific rotatory power lower than that ascribed to it (*loc. cit.*).

The picrate of *d*-coniine crystallises in small, yellow prisms, and melts at 75°. The aurochloride melts at 77°; the golden-yellow crystals of this salt belong to the rhombic system, the axial ratio being 0·3822 : 1 : 1·2221. The hydrochloride melts at 217·5—218 5°, the hydrobromide at 211°, and the hydriodide at 165°, the cadmio-iodide melting at 118°. The acid tartrate melts at 54°.

<div align="right">M. O. F.</div>

Constitution of Nicotine. By F. BLAU (*Ber.*, **27**, 2535—2539; compare Abstr., 1893, i, 489).—The author's previous work on this subject has proved that nicotine consists of a pyridine nucleus combined with a closed chain containing a nitrogen atom linked to a methyl group; whilst Pinner regards it as a methylpyrrolidine trimethyleneimine ring, he believes it to be an ethyleneimine ring, and, at present, it is impossible to decide definitely between these views.

Isodipyridine, prepared by Cahours and Étard by the oxidation of nicotine, is termed by the author *nicotyrine*, and is more readily obtained by acting on nicotine with moist silver oxide; its purification is. somewhat difficult. It boils at 149° (150° corr.; 15 mm.), and at 273—274° (280° corr.; 744 mm.). The yield is about 16 per cent. of the nicotine employed, of which about 38 per cent. is recovered. The iron reaction, mentioned by Cahours and Étard, is not characteristic for this base; it gives a dark coloration with isatin and sulphuric acid; a pine-wood splinter moistened with the base and then treated with hydrochloric acid is coloured dirty bluish-green, but the reaction is not very delicate. The base combines with 1HCl; the *picrate*, $C_{10}H_{10}N_2,C_6H_3N_3O_7$, is crystalline, and melts at 163—164°. The platinochloride decomposes at 120°; it is doubtful whether it contains $1\frac{1}{2}H_2O$ or $2H_2O$. The *methiodide*, $C_{10}H_{10}N_2MeI$, crystallises in lustrous, pale yellow needles, melting at 211—213°. The *ethiodide* resembles the preceding compound, and melts at 173·5—174·5°. In spite of many attempts under varied conditions, these were the only additive compounds of nicotyrine and methylic iodide or ethylic iodide which could be obtained; nicotyrine appears, therefore, to be a pyrroline

derivative, $C_5NH_4\cdot C\underset{\diagdown NMe\diagup}{\overset{\diagup CH-}{\underset{}{-CH-}}}CH$; this accords with its production

from nicotine better than such a formula as

$$C_5NH_4\cdot CH{:}C\underset{NMe}{\overset{-CH}{<}}{>}CH.$$
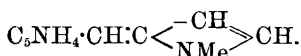
Attempts to eliminate the quaternary pyridine nucleus from nicotyrine by oxidation, and by fusion with potash, were unsuccessful.

In continuation of his investigations on the estimation of alkyl groups linked to nitrogen (this vol., ii, 219), Herzig finds that both hexahydronicotine and octohydronicotine contain a NMe-group.

<div align="right">J. B. T.</div>

Cinchotine or Hydrocinchonine. By W. KOENIGS and J. HOERLIN (*Ber.*, **27**, 2290—2292).—*Cinchotine chloride*, $C_{19}H_{23}N_2Cl$, is obtained by treating cinchotine hydrochloride with phosphorus pentachloride in chloroform solution. It crystallises well from ether and melts at 85—87°.

Dihydrocinchine, $C_{19}H_{22}N_2$, is obtained by boiling the preceding compound with alcoholic potash in a reflux apparatus. It crystallises in beautiful, white leaflets, melts at 145°, and, when heated with aqueous phosphoric acid at 170—180°, yields cincholeupone and lepidine. The *picrate* melts at 195°. It is therefore identical with the dihydrocinchene obtained from commercial cinchonine.

Cinchotine, when oxidised with chromic acid solution, yields cincholeupone which melts and decomposes at 236°, and yields a hydrochloride melting at 198—200°, and an aurochloride melting and decomposing at 203°. The authors were unable to detect cincholeuponic acid amongst the products of oxidation. E. C. R.

Isobutylcinchonine Hydrobromide. By F. VIAL (*J. Pharm.*, [5], **30**, 52—55).—Cinchonine (10 parts), isobutylic bromide (5 parts), and isobutylic alcohol (10 parts) are heated in a sealed tube at 100°. The product of the action is distilled in a current of steam, the residue extracted with water, and the concentrated solution set aside to crystallise. The solution of the crude crystals may be freed from the accompanying red colouring matter by extraction with chloroform.

Isobutylcinchonine hydrobromide, $C_{19}H_{21}N_2O \cdot C_4H_9$,HBr $+$ H_2O, forms colourless orthorhombic crystals, the full measurements of which are given; when dehydrated, it melts at 176°; it dissolves in water and in alcohol, but not in ether or chloroform. Its rotatory power in aqueous solution is $\alpha_D = + 125°$ ($p = 1$ in $100 \ v$; $t = 17°$). A. G. B.

The Methylbetaïne of Anhydroecgonine. By A. EINHORN and R. WILLSTÄTTER (*Ber.*, **27**, 2439—2454).—The substance supposed (Abstr., 1893, i, 378) to be paradimethyldihydrobenzylaminecarboxylic acid cannot have this constitution, for its methiodide, when boiled with aqueous soda, yields not trimethylamine, but dimethylamine. It is probably the methylbetaïne of anhydroecgonine, with the formula given below; when it unites with hydrogen iodide or methylic or ethylic iodide, the anhydride ring is broken, and the methiodide of anhydroecgoninic acid, or of its methylic or ethylic salt, is formed. This change in its formula necessitates similar changes in the formulæ of other allied compounds; these new formulæ are given below, the old name, when it differs from the new one, being enclosed in brackets. Cocaïne hydriodide, it may be said, probably stands in the same relation to benzoylecgonine as the methiodide of methylic anhydroecgoninate does to anhydroecgonine methylbetaïne.
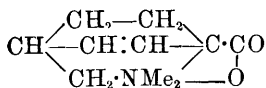
CH₂—CH₂
CH‹—CH:CH—›C·CO
CH₂·NMe₂——O

Anhydroecgonine methylbetaïne.
(Paradimethyldihydrobenzylaminecarb-
oxylic acid.)

CH₂—CH₂
CH‹—CH:CH—›C·COOMe
CH₂·NMe₂I

Methiodide of methylic anhydroecgo-
ninate.

CH₂—CH₂
CH‹—CH:CH—›C·CO
CH₂·NHMe——O

Anhydroecgonine.

CH·CH₂
C‹CH:CH›C·COOH
—CH₂—

Paramethylenedihydrobenzoic
acid.

CH₂——CH₂
CH‹CH₂·CH(OH)›C·CO
CH₂—NHMe——O
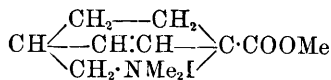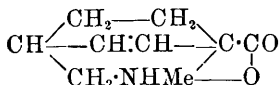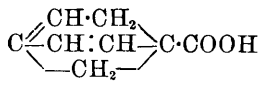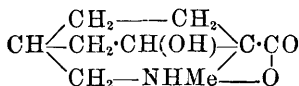
Ecgonine.

The compound formed by the addition of methylic iodide to an-
hydroecgoninemethylbetaïne is identical with the methiodide of
methylic anhydroecgoninate; when boiled with aqueous soda, it yields
dimethylamine. When the methylbetaïne is heated with ethylic
iodide, the main product is identical with the methiodide of ethylic
anhydroecgoninate, but, doubtless owing to the action of some hy-
driodic acid formed by a secondary reaction, some of the methiodide of
anhydroecgoninic acid itself is produced; this is the sole product
when the methylbetaïne is heated with ethylic iodide in absolute
alcoholic solution. When the methylbetaïne is heated with absolute
alcohol and sulphuric acid, and the product saturated with potassium
carbonate, being carefully cooled during the operation, there are
formed an oily base soluble in ether, not yet fully investigated, and
a neutral substance, insoluble in ether. The latter still contains a
NMe₂- and a COOEt-group, together with the anhydroecgonine ring,
for potassium carbonate decomposes it into dimethylamine and
ethylic paramethylenedihydrobenzoate; hydrochloric acid converts
it, at the ordinary temperature, into the methochloride of ethylic
anhydroecgoninate, and at the temperature of the water bath, into
alcohol and the methochloride of anhydroecgoninic acid; hydriodic acid
forms the methiodide of ethylic anhydroecgoninate. If, in the above
reaction, the saturation with potassium carbonate is carried out
without cooling being resorted to, the nitrogenous substance is at
once decomposed into dimethylamine and *ethylic paramethylenedi-
hydrobenzoate;* this boils at 225—227°, and is attacked by potas-
sium permanganate in the cold, differing in this respect from its
isomeride, ethylic paratoluate, which boils at the same temperature.

C. F. B.

Ergot of Rye. By KELLER (*J. Pharm.*, [5], **30**, 67—70).—
The author is of the opinion that there is but one alkaloïd in ergot
of rye, for the properties of the sole alkaloïd which he could obtain
proved to be identical with those of Tanret's ergotinine, Blumberg's
picrosclerotine, and Kobert's cornutine. He therefore proposes that

cornutine be retained as the name for this alkaloïd, and that the other words be expunged from chemical literature.　　　A. G. B.

Hydrolysis of Nucleïc acids. By A. KOSSEL and A. NEUMANN (*Ber.*, **27**, 2215—2222; compare this vol., i, 156).—When adenylic acid, prepared from the thyroid gland of the calf, is heated at 150° with 20 per cent. sulphuric acid, it is converted into thymin, a new base cytosine, ammonia, levulinic acid, formic acid, and phosphoric acid. Thymin, when quite pure, has the molecular formula $C_5H_6N_2O_2$, and not the more complicated formula $C_{23}H_{26}N_8O_6$, which was previously assigned to it.

Cytosine, $C_{21}H_{30}N_{16}O_4 + 5H_2O$, is precipitated by phosphotungstic acid, and crystallises from a faintly ammoniacal solution in rectangular tablets. It is readily soluble in hot water, very sparingly in alcohol, and insoluble in ether. The water of crystallisation is completely lost at 100°. The *sulphate* of the base crystallises in needles, the *hydrochloride* in prisms, whilst the *nitrate*, *platinochloride*, and *aurochloride* are also crystalline. Potassium bismuthoiodide produces a brick-red precipitate with dilute solutions of this base, whilst silver nitrate gives a precipitate which dissolves in hot dilute ammonia, and crystallises out on cooling. The *picrate*, $C_{21}H_{30}N_{16}O_4,2C_6H_3N_3O_7$, forms yellow needles. The yield of cytosine amounts to about 2 per cent. of the nucleïc acid employed.

The presence of levulinic acid among the products of decomposition is significant, and shows that adenylic acid contains a carbohydrate group. This is in agreement with the result obtained by Kossel in the case of the nucleïc acid prepared from yeast.　　　A. H.

Vegetable Proteïds. By W. PALLADIN (*Zeit. Biol.*, **31**, 191—202). —An examination of the various vegetable proteïds described by Weyl, Vines, Martin, Green, Chittenden, Osborne and others, leads the author to the following general conclusions:—

1. Plant-vitellin has many of the properties of albumoses.
2. Plant-myosin is only a calcium compound of vitellin.
3. The existence of vegetable albumoses soluble in water is questionable.
4. Vegetable proteïds are accompanied by a still unknown nitrogenous substance.
5. The number of hitherto described vegetable proteids is greater than the number which really exist in the plants.

　　　W. D. H.

JOURNAL

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Influence of Halogens on the Optical Values of Double Bonds. By G. CARRARA (*Gazzetta*, **23**, ii, 1—7).—The author is determining the refraction constants of a number of unsaturated aliphatic halogen derivatives, with the object of finding an explanation of the anomalous refraction of such substances as dibromacetylene and trib·omethylene. In the present paper he gives the following measurements of the refractive powers of monobromethylene and iso-α-bromopropylene.

Monobromethylene.—Sp. gr. at $4°/4° = 1·56558$; $\mu_{H_\alpha} = 1·44276$; $\mu_D = 1·44622$; $\mu_{H_\beta} = 1·45496$; $\mu_{H_\gamma} = 1·46251$;

$$\frac{P(\mu_{H_\alpha} - 1)}{d} = 30·26. \qquad \frac{P(\mu_{H_\alpha}^2 - 1)}{d(\mu_{H_\alpha}^2 + 2)} = 18·10.$$

Iso-α-bromopropylene.—Sp. gr. at $14·6°/4° = 1·43227$; $\mu_{H_\alpha} = 1·45189$; $\mu_D = 1·45536$; $\mu_{H_\beta} = 1·46374$; $\mu_{H_\gamma} = 1·47082$;

$$\frac{P(\mu_{H_\alpha} - 1)}{d} = 38·18. \qquad \frac{P(\mu_{H_\alpha}^2 - 1)}{d(\mu_{H_\alpha}^2 + 2)} = 22·82.$$

The differences between the observed and theoretical values, calculating both for saturated and unsaturated compounds, are considerable, varying from 0·5 to 1·4 units. W. J. P.

Abnormal Increase in the Refractive Power of Aromatic Bases. By F. ZECCHINI (*Gazzetta*, **23**, ii, 42—46).—The author has measured the refractive powers of diphenylamine and triphenylamine in benzene solution for the line N_{α}; the values obtained are very high, and give abnormally high values for the atomic refraction of nitrogen. The results are summarised in the following table, and compared with those obtained for aniline by Gladstone; it is noteworthy that the latter observer found that the atomic refraction of nitrogen in the homologous derivatives of aniline increased as the series was ascended.

Substance.	$P\dfrac{\mu_D - 1}{d}$.	$P\dfrac{\mu_D^2 - 1}{(\mu_D^2 + 2)d}$.	Atomic refraction of nitrogen.	
			From μ_D.	From μ_D^2.
NH_2Ph	53·37	30·56	7·46	3·38
$NHPh_2$	102·04	57·62	14·56	6·41
NPh_3	149·40	84·46	20·49	9·22

The measurements were made at 11—14°, and in solutions containing 9—17 per cent. of the bases. W. J. P.

Cause of the Variation of the Rotatory Power of the Solutions of certain Optically Active Substances. Rotatory Power of Amorphous Substances. By A. BÉCHAMP (*Bull. Soc. Chim.*, [3], **9**, 511—529).—It is well known that when glucose crystallised in nodules is dissolved in water, the rotatory power of the solution gradually diminishes, at last becoming little more than half its initial value. The author finds that glucose crystallised in nodules, and obtained by the saccharification of starch, contains a small quantity of dextrin insoluble in alcohol of 93°, and with a high rotatory power, $[\alpha]_j = +125°$; after this is removed, the alcoholic solution gradually deposits glucose in groups of small crystals with distinct faces. These have the composition $C_6H_{12}O_6 + H_2O$, and when dissolved in water the initial rotatory power is $[\alpha]_j = +96·4°$; but the rotatory power gradually diminishes, and after 24 hours becomes constant with the value $[\alpha]_j = +52\ 04°$. If these values are calculated to anhydrous, instead of to hydrated, glucose, they become respectively $+106\ 04°$ and $+57·23°$.

If the hydrated glucose is dried at 100°, and then dissolved in water, the solution has at once the rotatory power $[\alpha]_j = +57·6°$. If also after the rotatory power of a solution of hydrated glucose has become constant, the liquid is evaporated, and the residue is dissolved in water, the rotatory power is likewise $+57°$. It would seem, therefore, that the initial rotatory power of the solution of crystallised glucose is due to the hydrate, whilst the final value is due to anhydrous glucose, dehydration having taken place in solution.

If the crystallised glucose is heated in a current of dry air at about 60°, dehydration takes place without fusion as at 100°; but, never-

theless, when the anhydrous glucose is dissolved in water, the rotatory power has the higher value, and only becomes $+57°$ after some time. It would seem, therefore, that although crystallised glucose is not birotatory, anhydrous glucose has this property, and exists in two distinct modifications.

Glucose dehydrated with fusion at $100°$, or obtained by evaporation of a solution with the rotatory power $+57°$, melts at $100°$, and is a soft and truly amorphous mass which absorbs moisture from the air, and cannot be crystallised, whereas glucose dehydrated without fusion does not melt at $100°$, remains hard, retains its crystalline appearance, and absorbs moisture from the air without deliquescence, again producing the hydrate, $C_6H_{12}O_6 + H_2O$. In fact, if water is added to the dehydrated substance, combination takes place with development of heat. It follows that the higher rotatory power observed is due to the hydrate.

The rotatory power $+57°$ is due to anhydrous glucose which exists in the solution in an amorphous form, and it follows that optical activity is not necessarily connected with crystalline form.

The author suggests that, as a rule, compounds exist in both an amorphous and a crystalline form, although in many cases the crystalline modification is very difficult to obtain, and only the amorphous form is known. Amongst the latter may be mentioned the amyloses, cellulose, proteïds, &c.

The potassium compound of soluble starch has immediately after dissolution a rotatory power of $[\alpha]_j = +188·3°$, but if the solution is gradually diluted, the rotatory power increases, and tends to approach that of soluble starch itself, $+212°$. The potassium compound dissociates as the degree of dilution increases, but both it and the soluble starch are amorphous.

As examples of other substances that are unquestionably amorphous as usually obtained, the author mentions lignodextrin, obtained by the action of hydrochloric acid on cellulose; viscose, from saccharose, $[\alpha]_j = +224°$; osseïn, dissolved in hydrochloric acid, $[\alpha]_j = -411·6°$; osseïn soluble in water, $[\alpha]_j = -359·8$ at $11°$, but varying greatly with the temperature, and becoming only $-168°$ to $-177°$ at $30°$; gelatin, soluble "cartilageïn," the products of the gastric digestion of osseïn and gelatin. It is noteworthy that the rotatory power of almost all these solutions diminishes very considerably as the temperature rises.

A solution of very active diastase gave a rotatory power of $[\alpha]_j = -114·1°$, and this remained the same after boiling, although the diastatic power had been destroyed. In a similar manner, a solution of zythozymase retains its optical activity after boiling, although it has lost its power of fermenting saccharose.

It seems clear, therefore, that many substances which have never been crystallised have a marked optical activity; but this is not observed in solution only, for a film of gelatin has a marked rotatory power.

Optical activity is not necessarily connected with crystalline form, but depends chiefly on the chemical constitution of the molecules of the active substances. C. H. B.

2—2

Chemical Potential of Metals. By W. D. BANCROFT (*Zeit. physikal. Chem.*, **12**, 289—297).—The author has investigated the difference of potential between the metals magnesium, zinc, cadmium, tin, lead, bismuth, mercury, and platinum in various salt solutions. He finds that when the pairs of metals are selected from magnesium, zinc, cadmium, tin, lead, and bismuth, neither the positive nor the negative ion of the salt solution has any effect on the electromotive force, which also remains constant although the dilution varies from 10 to 1000 litres. When mercury forms one pole of the combination, the influence of the negative ion of the salt solution is very marked, but concentration does not influence the electromotive force. In the case of platinum, the difference of potential depends on the concentration of the salt solution when the dissolved salt is a haloïd. This is possibly due to the tendency of platinum to form platinochlorides, &c., in which the platinum is not present as an ion.

It would appear, although the numerical agreement still leaves something to be desired, that the electromotive force of the combination $M_1 \mid RX \mid M_2$ is identical with that of the reversible combination $M_1 \mid M_1X \mid M_2X \mid M_2$.   J. W.

Electromotive Forces of Polarisation. Part II. By M. LE BLANC (*Zeit. physikal. Chem.*, **12**, 333—358; compare Abstr., 1891, 1405).—From a further study of the electromotive forces of polarisation in salt solutions, the author finds that at the decomposition point in a solution from which a metal is deposited on the cathode, the electromotive force of polarisation at this electrode is equal to the electrolytic solution pressure of the metal in the solution, and is independent of the nature of the electrode, provided it is not attacked. The numerous apparent exceptions to this simple rule are referred by him to the development of gases at the electrodes, in which case the electromotive force necessary for their liberation depends in great measure on the nature and condition of the electrodes employed. By suitable arrangement of his apparatus, he was able to show that in many of these cases the solutions exhibited the normal behaviour, and that the electrolytic decomposition and formation of water (by means of a gas battery) is a reversible process. Salts of zinc, cobalt, nickel, and cadmium have a high decomposition point, and usually deposit the metal without evolution of hydrogen. This behaviour is due to special circumstances, and it is shown that under appropriate conditions hydrogen appears at the cathode, and not the metal.

The assumption that the atoms of gases contain a greater amount of energy than the molecules is considered by the author to be untenable. They form two states of matter with practically the same energy content, the difference between them being that the atoms enter into chemical action with a great velocity of reaction, which is only approached by the molecules when a catalyst is present.

J. W.

Electromotive Forces of Insoluble and Complex Salts. By K. ZENGELIS (*Zeit. physikal Chem.*, **12**, 298—313).—Ostwald obtained results for silver salts in agreement with the following general prin-

ciples :—Insoluble and complex salts, on account of the small concentration of their metallic ions, show considerable deviations from the calculated value of the electromotive force of two-fluid combinations in which they occur, the deviation increasing with the decreasing solubility of the salt. Salts soluble in the complex compounds have a smaller deviation, and salts insoluble in them a greater deviation, than the complex compounds themselves. The author has tested the validity of these rules, in the case of a number of slightly soluble and complex compounds of silver, copper, lead, nickel, and cobalt, and has obtained results in harmony with them.

In the case of the phosphates of lead, cadmium, and silver, the electromotive force gradually diminishes on standing, owing probably to the formation of basic salts. Similar diminutions were observed with the carbonates, and to a smaller extent with the arsenates. Where no basic salt is formed, as in the case of silver carbonate, the electromotive force remains constant. With sulphides, an increase of the electromotive force was sometimes noticed. probably due to the transformation of the hydrosulphides at first formed into normal sulphides. J. W.

Secondary Heats of Galvanic Elements. By H. JAHN (*Ann. Phys. Chem.*, **50**, 189—192).—The author gives the following corrected numbers for secondary heats of galvanic elements.

Element.	Secondary heat.	
	Found.	Calculated.
	Cal.	Cal.
$Cu,Cu(C_2H_3O_2)_2 \parallel Pb(C_2H_3O_2)_2,Pb$	$-4\cdot151$	$-4\cdot784$
$Ag,AgCl \parallel ZnCl_2 + 100H_2O,Zn$	$+5\cdot139$	$+5\cdot082$
$Ag,AgCl \parallel ZnCl_2 + 50H_2O,Zn$	$+2\cdot620$	$+2\cdot609$
$Ag,AgCl \parallel ZnCl_2 + 25H_2O,Zn$	$+2\cdot654$	$+2\cdot51$
$Ag,AgBr \parallel ZnBr_2 + 25H_2O,Zn$	$+1\cdot488$	$+1\cdot326$

He also replies to some objections raised by Streintz (*Ann. Phys. Chem.*, [2], **49**, 564) as to his method. J. W.

Properties of Mixtures of Amines and Acids. By D. KONO-VALOFF (*Ann. Phys. Chem.*, [2], **49**, 733—760).—In this paper, the author studies the electrolytic conductivity, freezing point, heat of solution, heat of dilution, and specific heat of mixtures of feeble bases, such as aniline and acids of the acetic series. An account of most of his conductivity experiments has already been published (compare Abstr., 1893, ii, 356). He formulates his conclusions as follows :—

1. Solutions formed by amines and organic acids are conductors of about the same order as solutions of organic acids in water.

2. At a high, but not infinite, dilution the conductivity of the solutions becomes infinitely small.

3. The curves which represent the electrical conductivity of these

solutions as dependent on the percentage composition, are not sym-
metrical. The maximum lies on the side of the liquid with smaller
molecular weight and volume, and to an extent which is determined
by the differences between the molecular weights (and the molecular
volumes) of the two liquids.

4. The curves near the x-axis are mostly concave, and the concavity
is greater, as the molecular weight and volume of the dissolved sub-
stance in comparison with those of the solvent is greater.

5. The peculiar behaviour of aqueous solutions appears to be due
principally to the small molecular weight and volume of the solvent.

6. The conductivity curves for mixtures of aniline and acetic acid
exhibit a series of singular points, corresponding with solutions of
simple multiple proportions.

7. The conductivity of liquids at the ordinary temperature is called
into play by chemical affinity between the dissolved electrolyte and
the excess of the solvent. The special condition of the unstable com-
pounds thus brought into existence favours chemical transformation,
without which no electrolytic conductivity is possible.

The curves for the heats of solution against percentage composi-
tion have maxima which in no case corresponds with the ratio of
1 mol. acid to 1 mol. amine, but is always on the side of the solutions
with excess of acid. The heat of dilution of the solution by the acid
is always positive, whilst, with an amine as the diluent, heat is de-
veloped up to a certain point, after which it is absorbed.

The depression of the freezing point of acetic acid by aniline is
normal for dilute solutions.   J. W.

Melting Points of Inorganic Salts. By V. MEYER and W.
RIDDLE (*Ber.*, **26**, 2443—2451).—The authors have commenced this
work in the hope of finding relations between the melting points of
inorganic salts similar to those known to exist between the melting
points of organic compounds.

The method employed consists in melting the salt in a platinum
crucible, and determining the solidifying point, by means of the
platinum air-thermometer described by V. Meyer and Freyer. Test
experiments with tin, lead, zinc, naphthalene, and anthraquinone
gave correct numbers.

At present the following melting points have been observed:—
Sodium chloride, 851°; sodium bromide, 727°; sodium iodide, 650°;
potassium chloride, 766°: potassium bromide, 715°; potassium
iodide, 623°; potassium carbonate, 1045°; sodium carbonate, 1098°;
borax, 878°; sodium sulphate, 843°; potassium sulphate, 1073°.

                                                        E. C. R.

Molecular Volumes of Boron Compounds. By A. GHIRA
(*Gazzetta*, **23**, ii, 8—11).—The author has determined the molecular
volumes of a number of liquid compounds of boron; the results are
given in the following table (p. 7).

The molecular volumes of water, given in column 4, are calculated
from the values concerned in the reaction by which the boron com-
pounds are obtained. Twice the observed molecular volume of the sub-
stance is subtracted from the sum of boric anhydride, and six times the

Substance.	d at 4°.	Mol. volume at 0°.	Mol. volume of water.
BCl$_3$	1·43386	81·94	—
BBr$_3$	2·64985	94·72	—
B(OEt)$_3$	0·88633	164·72	17·0
B(OC$_4$H$_9$$^\beta$)$_3$	0·86437	266·09	16·6
B(OC$_5$H$_{11}$$^\beta$)$_3$	0·87112	312·24	17·8
B(OC$_3$H$_5$)$_3$	0·94209	193·19	17·2

molecular volume of the alcohol used in the preparation; this differ-
ence, divided by three, gives the molecular weight of water. The
agreement is thus seen to be satisfactory. The molecular volumes of
consecutive members of the homologous series differ by about 16 units
for each increment of CH$_2$, as has been shown for other series by
Horstmann (Abstr., 1886, 750). W. J. P.

**Electrolytic Determination of the Solubility of Slightly
Soluble Substances.** By F. KOHLRAUSCH and F. ROSE (*Ann. Phys.*

Salt.	Salt contained at 18° in 1 litre in		Approximate temperature co-efficient at 18°.
	Milligram equivalents.	Milligrams.	
Silver chloride	0·0117	1·7	0·052
„ bromide..............	0·002	0·4	(0·023)
„ iodide	0·0006	0·1	—
Mercurous chloride..........	0·013	3·1	0·049
Mercuric iodide..............	0·002	0·5	—
Cuprous iodide..............	0·04 ?	8·0 ?	—
Cuprous thiocyanate..........	0·004 ?	0·5 ?	—
Calcium sulphate.............	0·35	14·0	0·007
Barium sulphate	0·022	2·6	0·018
„ „ (heavyspar)..	0·025	2·9	0·017
Strontium sulphate..........	1·16	107·0	0·000
Calcium sulphate.............	30·5	2070·0	0·003
Lead sulphate	0·30	46·0	0·007
Barium oxalate	0·66	74·0	0·021
Strontium oxalate	0·51	45·0	0·018
Calcium oxalate	0·092	5·9	0·016
Barium carbonate...	0·24	24·0	0·013
Strontium carbonate..........	0·15	11·0	0·015
Calcium carbonate	0·26	13·0	0·008
„ „ (arragonite)	0·30	15·0	0·008
Lead carbonate	(0·025)	(3·0)	0·009
Silver chromate	0·17	28·0	0·032
Barium chromate	0·03	3·8	0·023
Lead chromate	0·001	0·2	—
Magnesium hydroxide	0·41	9·0	0·000

Chem., [2], **50**, 127—137; compare Abstr , 1893, ii, 519).—The values given in the table, p. 7, for the solubility in water of so-called "insoluble" salts are calculated from determinations of the electric conductivity of the saturated solutions.   J. W.

Solubilities. By A. ETARD (*Bull. Soc. Chim*, [3], **9**, 82—87). — The author regards the curve of solubility as the locus of the melting points of mixtures of the dissolved substance and the solvent (Abstr., 1889, 460). In order to obtain the complete curve, the solubilities must be expressed, not as the amount of substance dissolved by 100 parts of the solvent, but as the amount contained in 100 parts of the saturated solution. The complete curve cannot, for obvious reasons, be obtained in the case of the majority of solutions of inorganic salts in water; and, therefore, the author has turned his attention to the solubilities of organic compounds in organic solvents. Complete solubility curves are given for several cases of this kind. Attempts were made, by the use of solvents melting at low temperatures, to obtain cases in which the solubility was ultimately reduced to zero, but without positive success. Chloroform (m. p. —68°) at —50° still dissolves considerable quantities of naphthalene and triphenylmethane. In most cases. however, the different solubility curves converge at low temperatures into a single line, the direction of which is towards the ordinate zero at the melting point.   H. C.

The Colour of the Ions. By J. WAGNER (*Zeit. physikal. Chem.*, **12**, 314—321).—Magnanini (Abstr., 1893, ii, 510) has stated that violuric acid when dissolved in pure water is colourless, and that the colour of its salts in aqueous solution cannot be attributed to a coloured negative ion. The author has repeated Magnanini's experiments with the acid, but has failed to obtain a colourless solution, water carefully freed from alkali always giving a violet liquid. He further finds that the absorption of solutions of the acid and the sodium salt is proportional to the number of violuric ions in the solution, as determined by the electrical conductivity. The absorption of the acid does not decrease proportionally to the dilution, as it should if the presence of a salt as impurity were the cause, but to the square root of the dilution, that is, proportionally to the number of negative ions. The decolorisation by means of other acids proceeds according to the law of isohydric solutions. A chromolithographic table of the colours of 16 solid violurates is given; these show great differences in colour, but when dissolved in water and sufficiently diluted, they all give violet solutions (due to the negative ion), provided the positive ion is colourless.   J. W.

Saline Solutions. By C. CHARPY (*Ann. Chim. Phys.*, [6], **29**, 1—68).—With a view of further elucidating the question as to the condition of a dissolved salt and its relation to the solvent, the author has determined, with all possible accuracy, the densities of a number of aqueous solutions of inorganic salts and organic acids of various concentrations. From these, the contraction was calculated, it having been already shown (Abstr , 1892, 1146) that the density is a linear

function of the contraction. The coefficient of contraction is given by the equation

$$K = \frac{1}{D}\left(1 + \frac{S}{D}\frac{dD}{dS}\right),$$

where S is the percentage composition of a solution of density D. The coefficient is always less than unity, so that dilution of a solution is always accompanied by a contraction. It diminishes with the concentration, so that a greater contraction is produced by diluting a concentrated than by diluting a dilute solution. It increases with the temperature, so that the contraction produced by dilution at a high temperature is smaller than that produced by dilution at a low one. If the concentration be expressed in terms of the ratio of the number of molecules of the dissolved compound to the number of molecules of the solvent, the curves representing the coefficient of contraction as a function of the concentration will take some simple form, and in any series of analogous compounds will be found arranged in the order of the magnitudes of the molecular weights. The last property is also characteristic of the curves obtained if the density is substituted for the coefficient of contraction. The curves in this case are linear in form, the density of a solution being a linear function of the concentration when the latter is expressed as above. This last result holds also for mixtures of salts in solution, and it is, therefore, possible to apply this law to the study of chemical equilibrium between salts in solution. H. C.

The Hydrate Theory. By W. MEYERHOFFER (*Ber.*, **26**, 2475—2478).—The author points out that the curves obtained by Pickering for the depression in freezing point in various solutions are in reality solubility curves, and reasons that since no breaks have hitherto been found in solubility curves unless the solid in equilibrium with the solution itself undergoes transformation, the breaks observed by Pickering have no real existence. J. W.

Equilibrium of Solutions with two and three Components. By H. W. B. ROOZEBOOM (*Zeit. physikal. Chem.*, **12**, 359—389).—The author gives a full theoretical discussion of the nature of the solubility curves for systems composed of two and of three components. An example of the equilibrium of a system of two components is to be found in the solubility relations of ferric chloride and its hydrates in water. Here the components are water and anhydrous ferric chloride; ice, the anhydrous salt, and the various hydrates form the solid phases, solutions of varying concentration forming the liquid phase. The solubility curves of the components are termed by the author side curves, the solubility curves of the hydrates (in this case *binary* compounds) being called intermediate curves. With systems of three components there may be *ternary* solid phases; for example, the hydrate of a double salt. The following tables exhibit the characteristic properties of the various curves and their points of intersection. The solid phases are denoted by S_1, S_2, &c., the liquid phase (solution) by L.

Characteristics of Solubility Curves.

Nature of curve.	Solid phases.	Direction of endothermic transformation at the maximum temperature of the curve.
A. Two Components.		
Side......................	One simple	$S \longrightarrow L.$
Intermediate	One binary	$S \longrightarrow L.$
B. Three Components.		
Side	Two simple...............	$S_1 + S_2 \longrightarrow L.$
	One simple + one binary...	$S_1 + S_2 \longrightarrow L,$ or
	Two binary	$S_1 \longrightarrow L + S_2.$
Intermediate	One simple + $\left\{\begin{array}{l}\text{containing}\\\text{together}\\\text{all three}\\\text{compo-}\\\text{nents}\end{array}\right.$ one binary Two binary	$S_1 + S_2 \longrightarrow L.$
	One simple + one binary. One binary + one ternary Two ternary $\left.\right\}$	$\left\{\begin{array}{l}S_1 + S_2 \longrightarrow L,\\\qquad\text{or}\\ S_1 \longrightarrow L + S_2.\end{array}\right.$

Points of Intersection.

Intersecting curves.	The intersection is a temperature minimum for	Direction of endothermic transformation at intersection.
A. Two Components.		
Two side...................	Both curves	$S_1 + S_2 \longrightarrow L.$
One side and one intermediate $\left.\right\}$	Both curves, or .... $\left.\right\}$	$S_1 + S_2 \longrightarrow L.$
Two intermediate	One curve	$S_1 \longrightarrow L + S_2.$
B. Three Components.		
Three side	Three curves	$S_1 + S_2 + S_3 \longrightarrow L.$
Two side and one intermediate One side and two intermediate Three intermediate ...... $\left.\right\}$	Three curves, or......... Two curves .... $\left.\right\}$	$S_1 + S_2 + S_3 \longrightarrow L.$ $S_1 + S_2 \longrightarrow L + S_3.$

J. W.

Temperature of Explosion of Mixtures of Gases. By V. MEYER and A. MÜNCH (*Ber.*, **26**, 2421—2432).—The explosion was effected in a glass vessel, situated inside the bulb of an air thermometer, the latter being immersed in a metal bath. The mixture of a gas with the amount of oxygen theoretically necessary for its complete combustion was passed through a fine tube to the bottom of the glass vessel, and lighted as it issued from the mouth of the tube which formed the upper continuation of the vessel. At a certain temperature the flame ran down the tube, and the contents of the vessel exploded. This temperature—the temperature of explosion—was then determined by displacing the air contained in the air thermometer with hydrogen chloride, collecting it over water, and measuring it.

A series of experiments was first made with hydrogen and oxygen. The temperature of explosion is not constant, but varied in 38 experiments from about 620° to 680°, being about 650° in the mean. It is not affected by variations in the rapidity with which the gases enter the glass vessel, or by the presence of glass splinters or sand. The presence of platinum prevents an explosion, the gases combining quietly, and if the glass vessel is very small no explosion occurs.

Some experiments were then made with carbonic oxide and with hydrogen sulphide, but these gases, for the most part, combined quietly with oxygen.

. The following aliphatic hydrocarbons were then examined, and found to have the following temperatures of explosion when mixed with oxygen. Methane, 656—678°; ethane, 605—622°; ethylene, 577—590°; acetylene, 509—515°; propane, 545—548°; propylene, 497—511°; isobutane, 545—550°; isobutylene, 537—548°; coal-gas (with three times its volume of oxygen), 647—649°. It would thus appear that the temperature of explosion falls as the number of carbon atoms in the molecule increases; that it is probably lower for primary than for the corresponding secondary hydrocarbons; and is less for hydrocarbons containing a double bond than for those containing only single bonds, and still less for those containing a triple bond.　　　　　　　　　　　　　　　　　　　　C. F. B.

Extraction Apparatus. By J. TCHERNIAC (*Ber.*, **26**, 2359).—A defence of the author's apparatus (Abstr., 1893, i, 229) for extraction with hot ether against the objections urged by Hagemann (*ibid.*, ii, 567).　　　　　　　　　　　　　　　　　　　　　　　　　C. F. B.

Inorganic Chemistry.

Hydrates of Hydrogen Iodide. By S. U. PICKERING (*Ber.*, **26,** 2307—2310).—In continuation of his previous work on the hydrates of hydrogen chloride (Proc., 1893, 45) and of hydrogen bromide (*Phil. Mag.*, 1893), the author has succeeded in isolating three

hydrates of hydrogen iodide. The *dihydrate*, $HI.2H_2O$, forms large crystals melting at about $-43°$. The *trihydrate*, $HI,3H_2O$, melts at $-48°$, and forms small, granular crystals. The *tetrahydrate*, $HI,4H_2O$, melts at $-36·5°$, and is deposited in large, transparent, granular crystals.

The numerical results are tabulated, and are also represented graphically in the form of curves. The following hydrates of hydrogen chloride and of hydrogen bromide are known. HCl,H_2O; $HCl,2H_2O$, m. p. $-17·4°$; $HCl,3H_2O$, m. p. $-24·8°$; HBr,H_2O; $HBr,2H_2O$, m. p. $-11·2°$; $HBr.3H_2O$, m. p. $-48°$; $HBr,4H_2O$, m. p. $-55·8°$. No simple relationship appears to exist between the melting points of the various hydrates of the three acids.   J. B. T.

Decomposition of Hydrogen Iodide by Heat. By M. Boden-stein (*Ber.*, **26**, 2603—2611; compare Abstr., 1893, ii, 369).—Further experiments have yielded the following numbers for the amount of hydrogen iodide decomposed at various temperatures.

290°	310°	320°	340°	350°	394°	448°	518°
0·164	0·167	0·160	0·171	0·176	0·196	0·214	0·236

A minimum appears to exist at 320°, at which temperature the heat of reaction is probably zero.

The influence of pressure is seen in the following table.

Pressure in atmospheres.	350°.	448°.	518°.
0·5	0·135	0·202	0·225
1·0	0·176	0·214	0·236
1·5	0·192	0·222	0·241
2·0	0·199	0·231	0·244

The constant C of the velocity equation for the decomposition varies as follows.

Pressure.	350°.	448°.
0·5	0·0000345	0·00266
1·0	0·0000699	0·00503
1·5	0·0001151	0·00820
2·0	0·0001571	0·01143

This table shows that the constant is very nearly proportional to the pressure.   J. W.

Action of Ammonia on some Peroxides. By O. Michel and E. Grandmougin (*Ber.*, **26**, 2565—2568).—When dry gaseous ammonia is passed over the heated peroxides of sodium, barium, manganese, and lead, the ammonia is oxidised to nitrogen, and the metal left either

as hydroxide (sodium and barium) or oxide (manganese sesquioxide, litharge). In addition to these products, in all cases except that of barium, a small amount of nitrous and nitric acids is formed.

A. H.

Properties and Constitution of Hydroxylamine and its Homologues. By W. BRÜHL (*Ber.*, **26**, 2508—2520). See this vol., i, 9.

Preparation of Nitrous Oxide. By W. SMITH (*J. Soc. Chem. Ind.*, **11**, 867—869; **12**, 10—11).—A mixture of ammonium sulphate and sodium nitrate, kept at 215° for 2—3 hours, undergoes, in great part, decomposition into sodium sulphate and ammonium nitrate. If, however, it is rapidly raised to a higher temperature, nitrous oxide begins to be evolved at 230°, and comes off with some rapidity at 240—250°. During the heating up a little ammonia is evolved, and the longer the mixture is kept at about 220—230°, the more ammonia is lost. If, then, the two salts have been mixed in molecular proportions, the deficiency in the ammonia leads to the evolution of some of the higher oxides of nitrogen towards the end of the reaction. This may be remedied by increasing the proportion of ammonium sulphate, the mixture, with an additional 5 per cent. of that salt, affording a larger yield of nitrous oxide than would be obtained from the equivalent quantity of ammonium nitrate. The gas is evolved with regularity, whereas ammonium nitrate, raised to 240°, decomposes with a rapidity accelerating towards explosive violence. M. J. S.

Hyponitrous acid. By A. THUM (*Monatsh.*, **14**, 294—310).—The author supports the theory of Dunstan and Dymond (Trans., 1887, 656), according to which, the first product of the reduction of sodium nitrite in alkaline solution is the sodium derivative of a dihydroxylamine, two molecules of which then condense to form sodium hyponitrite, (1) $Na_2 + 2H_2O + NaNO_2 = NaN(OH)_2 + 2NaOH$. (2) $2NaN(OH)_2 = Na_2N_2O_2 + 2H_2O$. This condensation seems to be favoured by the presence of an excess of alkali, for if this be neutralised by a current of carbonic anhydride, no hyponitrite is formed. The nitrogen evolved during the reduction is not due to the reduction of hydroxylamine, to which it has usually been ascribed, for this substance is scarcely attacked by sodium amalgam, but probably to a reaction between the dihydroxylamine and hydroxylamine, $NH_2 \cdot OH + NH(OH)_2 = N_2 + 3H_2O$. The preparation of hyponitrites by means of ferrous hydroxide has no advantage over the ordinary method of reduction by means of sodium amalgam.

Hyponitrous acid is also formed by the action of hydroxylamine on nitrous acid. About 2 per cent. of the theoretical amount of the silver salt is formed when equivalent solutions of hydroxylamine hydrochloride or sulphate and sodium nitrite are mixed, allowed to remain until the violent evolution of nitrous oxide has ceased, and then treated with a solution of silver nitrate. No hyponitrite is formed in alkaline solution. Further investigations are in progress as to the exact course of this reaction. Attempts to isolate hyponitrous acid from the dry silver salt by means of dry hydrogen

sulphide showed that even at low temperatures it is very unstable
and liable to explosive decomposition; the remaining experiments
were, therefore, made with solutions of the acid, prepared by act-
ing on the silver salt with the calculated amount of hydrochloric
acid. The solution is colourless and strongly acid, and is stable
towards dilute acids and alkalis even on boiling. On titration with
potash, in the presence of phenolphthaleïn or litmus, the solution
remains acid until the acid salt is formed, and then becomes alkaline.
The acid does not affect methyl-orange, and does not expel carbonic
anhydride from the alkali carbonates. In acid solution, it is quan-
titatively converted by potassium permanganate into nitric acid,
whilst in alkaline solution, nitrous acid is formed. Pure solutions of
the acid, contrary to the statements of Divers on the one hand, and
Van der Plaats on the other, do not decolorise solutions of iodine and
prevent the formation of iodide of starch, neither do they liberate
iodine from acid solutions of potassium iodide. Hyponitrous acid is
very stable towards reducing agents, both in the presence of acids
and alkalis. Solutions of the acid hyponitrites of the alkalis give pre-
cipitates with the salts of many metals. These metallic salts are
being further examined.

The Oxidation of Hydroxylamine.—When hydroxylamine is acted on
by alkaline permanganate, an amount of oxygen is taken up which is
exactly half way between the amounts required to convert the
hydroxylamine into hyponitrous acid on the one hand, and nitrous
acid on the other. This corresponds with the formation of a sub-
stance of the formula $H_2N_2O_3$, which bears the same relation to hypo-
nitrous acid that an azoxy- does to an azo-compound,

$$HO \cdot N \colon N \cdot OH. \qquad\qquad O <^{N \cdot OH}_{N\ OH}.$$

Hyponitrous acid (azohydroxyl).   Azoxyhydroxyl.
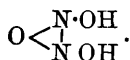
Experiments are in progress on the isolation of this substance.
Hydroxylamine is also oxidised by mercuric oxide, cupric oxide,
hydrogen peroxide, and alkaline potassium ferricyanide, small
amounts of hyponitrite being formed in each case. The greater part of
the nitrogen, however, is converted into nitrous oxide or nitrous acid.

<div align="right">A. H.</div>

[The paper by W. Wislicenus (Abstr., 1893, ii, 311) in which the
formation of hyponitrous acid by the interaction of hydroxylamine,
and nitrous acid is described was read at a somewhat later date than
the foregoing.]   A. H.

Rate of Oxidation of Hydrogen Phosphide. By H. J. VAN DE
STADT (*Zeit. physikal. Chem.*, **12**, 322—332).—When dry gaseous
hydrogen phosphide and oxygen are brought together at a low pres-
sure, they combine at once with emission of light to form phosphorous
acid according to the equation $2PH_3 + 3O_2 = 2H_3PO_3$. The appa-
ratus used by the author to determine the combining proportions
consisted of a pear-shaped bulb connected on the one hand with an
air-pump and manometer, and on the other with a gas pipette, by
means of which definite quantities of gas could be introduced. The

bulb was rendered vacuous, a certain number of measures of hydrogen phosphide admitted, and then oxygen, measure by measure, until the flash on combination no longer appeared. The manometer showed no change of pressure before and after the reaction.

When the gases were admitted very slowly from the pipette, an intermittent greenish-blue light was observed, and the manometer indicated that equal volumes of oxygen and hydrogen phosphide interacted, leaving an equal volume of a permanent gas as residue. When the mixing of the two gases was allowed to take place by diffusion at a pressure under 50 mm., accurate results were obtained, and the crystalline solid which was deposited on the walls of the bulb was proved to be metaphosphorous acid, formed according to the equation $PH_3 + O_2 = H_2 + HPO_2$. The crystals melt above 80°, and deliquesce in presence of a little water vapour, the solution shortly afterwards becoming solid again from formation of orthophosphorous acid.

Slow oxidation at greater pressures appears to proceed approximately according to the equation $4PH_3 + 5O_2 = 2HPO_2 + 2H_3PO_3 + 2H_2$. Dilution does not increase the rate of oxidation continuously, but, when a certain low pressure is reached, explosion takes place suddenly. The limiting pressure for explosion depends very greatly on the amount of moisture present, which, in this case, retards and prevents the oxidation, a result in direct contrast with those obtained by Baker and by Dixon for most cases of combination.

J. W.

Polymeric Thiocarbonyl Chloride. By G. CARRARA (*Gazzetta*, **23**, ii, 12—17).—By means of cryoscopic determinations in benzene solution, the author confirms the generally accepted view that the polymeride of thiocarbonyl chloride has the molecular composition $(CSCl_2)_2$; the thermometric depressions indicate a small but increasing amount of dissociation as the solutions become more dilute. The refraction constants of thiocarbonyl chloride, of its polymeride and of perchloromethylmercaptan were also determined for the α, β, and γ hydrogen lines and the D line; the principal results are given in the following table.

Substance.	t.	$P\dfrac{\mu_{H_\alpha} - 1}{d}$.	$P\dfrac{\mu_{H_\alpha}^2 - 1}{(\mu_{H_\alpha}^2 + 2)d}$.	Atomic refraction of sulphur.	
				From μ.	From μ^2.
$S{:}CCl_2$	9·0°	40·20	23·37	15·60	8·85
$S{:}CCl{\cdot}S{\cdot}CCl_3$ ..	$\begin{cases} 12·4 \\ 11·9 \end{cases}$	$\begin{matrix}76·54\\76·70\end{matrix}$	$\left.\begin{matrix}43·94\\43·94\end{matrix}\right\}$	13·71	7·45
$SCl{\cdot}CCl_3$	11·0	58·93	34·19	14·73	7·63

The measurements for the polymeric thiocarbonyl chloride were made on benzene solutions containing 16·139 and 15·549 per cent. respectively. It is noteworthy that the atomic refractions of sulphur

deduced from these observations are considerably smaller than those observed by Nasini and Costa with similar compounds.

<div align="right">W. J. P.</div>

Magnesium Nitride. By A. SMITS (*Rec. Trav. Chim.*, **12**, 198—202).—Magnesium nitride is prepared by heating magnesium powder in a current of dry ammonia. It is a yellow substance, easily powdered, and must be kept in sealed tubes, as it is rapidly acted on by the moisture of the air. Although immediately decomposed by water, it is not acted on by glycerol or by oxalic acid dissolved in absolute alcohol. Nitrate of silver in alcoholic solution is reduced.

A quantitive synthesis establishes the composition Mg_3N_2, a result confirmed by analyses.

<div align="right">W. T.</div>

Lead Tetrachloride. By H. FRIEDRICH (*Monatsh.*, **14**, 505—520; compare Abstr., 1890, 699; 1893, ii, 415; also Classen and Zahorski, *ibid.*, 1893, ii, 464).—The author confirms the formula $PbCl_4,2NH_4Cl$ for the double chloride of lead and ammonium, to which Classen and Zahorski (*loc. cit.*) gave the formula $2PbCl_4,5NH_4Cl$, and is of th · opinion that the compound analysed by those investigators contained free ammonium chloride. The behaviour of the double salt on adding it to well-cooled sulphuric acid, whereby lead tetrachloride separated as an oily substance, was so remarkable that the author investigated the behaviour of ammonium stannichloride towards sulphuric acid, and obtained a similar result, tin tetrachloride being formed. The tetrachlorides of lead and tin therefore closely resemble each other in regard to their stability in presence of sulphuric acid, and tin and germanium tetrachlorides may even be distilled from the concentrated acid without decomposition. On the other hand, the higher chlorides of iron and of antimony are readily decomposed by the acid with evolution of hydrogen chloride. Attempts to isolate lead tetrabromide or its double salt with an alkaline bromide have proved unsuccessful.

<div align="right">G. T. M.</div>

Basic Copper Selenate and Basic Cobalt Selenate. By BOGDAN (*Bull. Soc. Chim.*, [3], **9**, 584—586).—*Basic copper selenate*, $2SeO_3,3CuO,4H_2O$, or $Cu(O \cdot SeO_2 \cdot OCu \cdot OH)_2 + 3H_2O$, is obtained by heating a 10 per cent. solution of normal copper selenate in sealed tubes at 240—250° for several hours. It forms minute, transparent, emerald-green, prismatic crystals, insoluble in water but easily soluble in acids. When heated at about 250°, the salt loses water and decomposes with liberation of selenium. The fact that the salt does not lose water at 210° is not regarded by the author as evidence that the water is not present in the form of water of hydration.

Basic cobalt selenate, $3SeO_3,4CoO,H_2O$, or

$$OH \cdot CoO \cdot SeO_2 \cdot O \cdot CoO \cdot SeO_2 \cdot O \cdot CoO \cdot SeO_2 \cdot OCo \cdot OH,$$

is obtained in a similar manner, and forms small, red, acicular crystals strictly analogous to the copper compound in general properties.

<div align="right">C. H. B.</div>

Hydrogen compounds.	Lithium compounds.	Ammonium compounds.		Sodium compounds.	Potassium compounds.
—	MnCl₂,LiCl,3H₂O	MnCl₂,NH₄Cl,2H₂O	MnCl₂,2NH₄Cl,H₂O	—	—
—	FeCl₃,LiCl,3H₂O	—	FeCl₃,2NH₄Cl	—	FeCl₃,2KCl.
—	NiCl₂,LiCl,3H₂O	NiCl₂,NH₄Cl,6H₂O	—	—	—
CoCl₂,HCl,3H₂O	CoCl₂,LiCl,3H₂O	CoCl₂,NH₄Cl,6H₂O	—	—	—
CuCl₂,HCl,3H₂O	CuCl₂,LiCl,2½H₂O	CuCl₂,NH₄Cl	CuCl₂,2NH₄Cl,2H₂O	—	{ CuCl₂,2KCl,2H₂O. / CuCl₂,KCl.
CdCl₂,HCl,3½H₂O	CdCl₂,LiCl,3½H₂O	CdCl₂,NH₄Cl,½H₂O	—	—	CdCl₂,KCl,½H₂O.
SnCl₄,HCl,3H₂O	SnCl₄,LiCl,4H₂O	—	SnCl₄,2NH₄Cl	SnCl₄,2NaCl,5H₂O	SnCl₄,2KCl.

New Double Chlorides. By A. CHASSEVANT (*Ann. Chim. Phys.*, [6], **30**, 5—56 ; compare Abstr., 1892, 118 and 1275).—The author has prepared and analysed most of the double salts the formulæ of which appear in the table (preceding page) ; some of these are new, whilst others have already been described by himself and others. The arrangement renders clear the relations and differences which exist between the salts.   A. R. L.

Decomposition of Alkali Stannates under the influence of Carbonic Anhydride and of Alkali Carbonates. By A. DITTE (*Ann. Chim. Phys.*, [6], **30**, 282—285).—Austen has shown (*Chem. News*, **46**, 286) that stannic oxide may be readily prepared by passing a current of carbonic anhydride into a solution of an alkali stannate containing an excess of alkali.

When some bubbles of carbonic anhydride are allowed to fall on the surface of a dilute solution of an alkali stannate, a cloudy separation of gelatinous stannic oxide rises to the surface, and, as it increases in amount, the carbonic anhydride ceases to be absorbed. When, however, the carbonic anhydride is introduced very slowly in contact with crystals of stannate, a dense monohydrated stannic oxide is formed, which seems to be amorphous. If carbonic anhydride is passed into a mixture of stannate and carbonate, stannic oxide falls to the bottom of the liquid. Alkali carbonate free from the acid salt does not give rise to the production of stannic oxide when added to a stannate ; stannic oxide is formed in amount proportional to the quantity of acid salt present.   A. R. L.

Preparation of Potassium Metantimonate. By DUYK (*Chem. Centr.*, 1893, ii, 254 ; from *Bull. Soc. roy. Pharm. Bruxelles*, **37**, 109).—The method depends on eliminating the sulphur from the sulphantimonate by means of copper oxide. Black antimony sulphide (100 grams), potassium carbonate (150 grams), slaked lime (100 grams), and sulphur (20 grams) are shaken with 12 litres of water, and after remaining eight days the mixture is filtered. The filtrate, which contains potassium sulphantimonate, is boiled with copper oxide (120 grams) and filtered. The filtrate is diluted with water and treated with carbonic anhydride, when potassium metantimonate is precipitated.   E. C. R.

Mineralogical Chemistry.

Canfieldite, a new Germanium Mineral. By S. L. PENFIELD (*Amer. J. Sci.*, **46**, 107—113).—This new mineral was brought from Bolivia by F. A. Canfield. It crystallises in combinations of the octahedron and rhombic dodecahedron. The fracture is conchoïdal, the hardness 2·5, the sp. gr. 6·27, the colour black, the streak greyish-black, and the melting point very low. The mineral consists of

silver, germanium, and sulphur, and has the same quantitative composition as argyrodite. Analysis gave the following results:—

S.	Ge.	Ag.	Total.
17·10	6·57	76·33	100·00

Thus canfieldite and argyrodite have the same chemical composition, which is Ag_8GeS_6.

A new analysis, made by the author, of argyrodite from Freiberg gave

S.	Ge.	Ag.	Total.
16·83	6·69	76·48	100·00

The mineral Ag_8GeS_6 is therefore dimorphous, canfieldite being isometric and argyrodite monoclinic. B. H. B.

Natural Manganese Oxides: Polianite and Pyrolusite. By A. GORGEU (*Bull. Soc. Chim.*, [3], **9**, 496—502).—The author has examined a specimen of polianite from Platten, in Bohemia, and specimens of crystallised pyrolusite from many localities in Central and Eastern Europe. The hardness of the polianite was 6·5, and its sp. gr. 5·03 to 5·09; whilst the hardness of the pyrolusite varied from 2·5 to 5·0, and the sp. gr. from 4·75 to 5·10, according to the degree of hydration. Only the polianite was really anhydrous, and the proportion of water in the pyrolusite varied from 0·75 to 2·65 per cent., only about one-third being given off in a vacuum, and a further quantity at about 280°. The temperature of decomposition of the pyrolusites is above 460°, and is identical with that of the artificial varieties. When incompletely dissolved by hydrochloric acid, the residue has the composition of manganese peroxide. Boiling nitric acid, concentrated or dilute, dissolves only a trace of manganese.

The impurities in the pyrolusites are practically the same in all cases, namely, iron, calcium, magnesium, lead, barium, potassium, and sodium, and sulphuric, carbonic, phosphoric, and arsenic acids; they are present only in small proportion. The percentage of manganous anhydride, MnO_2, present after abstraction of the impurities varies from 98 to 100 per cent. C. H. B.

Rowlandite. By W. E. HIDDEN and W. F. HILLEBRAND (*Amer. J. Sci.*, **46**, 208—212).—About 2 lbs. of this mineral was found by W. E. Hidden, in a shipment of yttria-bearing minerals from Llano Co., Texas. The mineral is isotropic; its hardness is 6; its sp. gr. 4·513 at 15·5°; its fracture glassy-conchoïdal; its lustre vitreous-resinous; and its streak is greenish-grey. An analysis by W. F. Hillebrand gave the following results:—

SiO₂.	Ce₂O₃.	La group.	Y group.	FeO.	MnO.	MgO.	F.
26·04	5·06	9·34	47·70	4·39	0·67	1·62	3·87

These are in accord with the empirical formula $Si_4R_4'''R''F_2O_{14}$.

B. H. B.

3—2

Zoisite from North Carolina. By W. E. HIDDEN (*Amer. J. Sci.*, **46**, 154).—Very pure monazite at the Flat Rock mine, Mitchell Co., North Carolina, was found by the author to be surrounded by a pink, vitreous zoisite associated with a black, glassy allanite. An analysis of the zoisite gave the following results :—

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	H_2O.	Total.
39·98	31·02	4·15	0·23	23·80	2·03	100·21

The sp. gr. is 3·352 at 27°. B. H. B.

Mackintoshite, a new Thorium and Uranium Mineral. By W. E. HIDDEN and W. F. HILLEBRAND (*Amer. J. Sci.*, **46**, 98—103). —With thorogummite and cyrtolite in Llano Co., Texas, a new mineral has been discovered. It is opaque and black, but not quite so dull in lustre as the associated cyrtolite. A strong lens is necessary to distinguish the two. The hardness of the mineral is 5·5, and no trace of cleavage has been observed. The fracture is sub-conchoïdal to hackly, and the sp. gr. is 5·438 at 21°. Its form is tetragonal, and resembles zircon and thorite in habit and angle. Square prisms, sometimes 1 cm. thick, with a simple pyramid, are all the forms thus far observed. It also occurs massive, nodular, and filling veins in cyrtolite and fergusonite embedded in coarse pegmatite. It is infusible before the blowpipe, and is not entirely decomposed by any one acid. Analysis gave results in accord with the formula $UTh_3Si_3H_6O_{18}$, the formula of thorogummite being $UTh_3Si_3H_{12}O_{21}$. B. H. B.

Alnoite containing Melilite. By C. H. SMYTH (*Amer. J. Sci.*, **46**, 104—107).—The author described (Abstr., 1892, 1057) a small dyke occurring in a fault fissure at Manheim, New York. Recently some sections have been prepared from fresher material, and these show that one of the constituents is melilite, a supposition that the author originally hesitated to accept. Upon the basis of its mineralogical composition, and from a comparison with a specimen from Alnö, the rock must be classed as alnoite. The optical properties of the melilite are fully described, the mineral, although consisting chiefly of positive material, having patches of a negative character scattered through them. B. H. B.

Actinolite Magnetite Schists in Minnesota. By W. S. BAYLEY (*Amer. J. Sci.*, **46**, 176—180).—Attention has repeatedly been called to the existence of beds of amphibole schists associated with the ores in the older iron ore regions of the Lake Superior district. Consequently, their discovery on the newly opened Mesabi range is of interest from a theoretical standpoint. The descriptions of them given by the author agree very closely with those given by Irving and Van Hise (Abstr., 1892, 794) for the corresponding schists in the Penokee series, except that in the Minnesota rocks quartz is rare, and hæmatite is absent. The presence of these peculiar rocks in the Mesabi range is noteworthy, since their origin in other districts has

been thought to be closely connected with that of the iron ores with which they are associated. B. H. B.

Physiological Chemistry.

Oxidation of Methylic and Ethylic Alcohols in the Organism. By J. POHL (*Chem. Centr.*, 1893, ii, 380—381; from *Arch. Expt. Path. Pharm.*, **31**, 281—302).—Ethylic alcohol administered to a dog produces protracted sleep, and when this passes off, the dog awakes in a normal condition. Methylic alcohol, on the other hand, produces restlessness, giddiness, and then broken sleep; and the effects of a dose last for three or four days. A dog may be dosed without harm for a year with ethylic, isobutylic, or amylic alcohol; but with methylic alcohol death ensues in a few weeks.

In the case of poisoning by methylic alcohol, formic acid appears in the urine, and reaches a maximum on the third or fourth day.

E. C. R.

Presence of Ammonia in the Stomach, and its Influence on the Estimation of the Hydrochloric acid. By H. STRAUSS (*Chem. Centr.*, 1893, ii, 379—380; from *Berlin. Klin. Woch.*, **30**, 398—402). —The author confirms Rosenheim's results (Abstr., 1893, ii, 177).

The only method of estimating the chlorine which is not influenced by the presence of ammonium chloride is Leo's method; the free and combined hydrochloric acid is converted into calcium chloride by means of calcium carbonate, which does not decompose the acid phosphates, and the acidity is determined before and after this treatment. E. C. R.

Mineral Matter of Bones and Teeth. By S. GABRIEL (*Zeit. physiol. Chem.*, **18**, 257—303).—The mineral matters in bone and teeth contain lime, magnesia, potash, soda, water, phosphoric acid, carbonic anhydride, chlorine, and fluorine; there is, in addition, a substance which, when fused, turns red. The quantities of lime and phosphoric acid, which are the most abundant constituents, vary but little, and are proportional one to the other; the amounts of magnesia and carbonic anhydride are also proportional to each other. The amount of potash is greater than that of soda. The quantity of chlorine is very small, and is greater in the teeth (0·21 per cent.) than in bone. Fluorine is the minimal constituent of both (as a rule not over 0·05 per cent.), and is not more abundant in teeth than in bone.

Water is present in two forms : one part, passing off at 300—350°, is similar to water of crystallisation; the other part is only expelled by fusion with silicic acid, and is an expression of the basicity of the phosphate, and is called water of constitution or acidic water.

The bone phosphate has a basic character, containing 15 equivalents of acid to 16 of base; and it is probably a loose union of a

normal with a basic phosphate. The composition of the ash finds its simplest expression in the formula $Ca_3(PO_4)_2 + Ca_5HP_3O_{13} + Aq)$, in which 2 to 3 per cent. of the lime is replaced by magnesia, potash, and soda, and 4 to 6 per cent. of the phosphoric acid by carbonic anhydride, chlorine, and fluorine. The limit of variation is, however, small; and the differences between bone ash and tooth ash are not greater than those between the ash of different bones.

W. D. H.

Amount of Fluorine in Teeth. By E. WRAMPELMEYER (*Zeit. anal. Chem.*, **32**, 550—553).—The author employed Carnot's method (Abstr., 1892, 911), and obtained the following numbers.

Healthy teeth of adults........	1·37 per cent. of fluorine		
Diseased ,, ,, ...	1·16	,,	,,
Healthy ,, children......	0·65	,,	,,
Diseased ,, ,, ...	1·40	,,	,,

whence he infers that no direct conclusion as to the soundness of teeth can be drawn from the percentage of fluorine they contain.

Each sample of teeth consisted of 4 molars, 2 incisors, and 1 canine tooth. Test analyses with pure potassium silicofluoride gave 93·5 and 93·8 per cent.

M. J. S.

Chemistry of the Refractive Media of the Eye. By C. T. MÖRNER (*Zeit. physiol. Chem.*, **18**, 213—256; compare Abstr., 1893, ii, 424).—*The Cornea.*—This is considered in its separate layers. The *substantia propria* of the cornea was considered by Müller to consist of a chondrigenous substance similar to that found in hyaline cartilage. Morochowetz showed that chondrin, here as elsewhere, is not a chemical unit, but a mixture of gelatin with a mucinoïd material. This has been confirmed since then, and special attention is here paid to the mucinoïd material, which is here called *cornea-mucoïd.* It was extracted with dilute alkali, and precipitated from the extract by acetic or hydrochloric acid. Its percentage composition is C, 50·16; H, 6·97; N, 12·79; S, 2·07; O, 28·01. It closely resembles in its properties the mucoïds found in hyaline cartilage and the vitreous humor, and the pseudo-mucin of ovarian fluid. The gelatin obtained from the collagen, the other main constituent of the cornea, resembles that obtained from other sources. The mucoïd and collagen of the sclerotic are identical with those obtained from the cornea.

Only traces of pure proteïd matter are obtainable from the *substantia propria* of the cornea; the larger quantities previously described originated doubtless from the epithelial layer. This layer yields abundance of proteïd matter which very closely resembles paraglobulin in its properties. Nucleïn was not obtained, neither was any trace of myosin found. Descemet's membrane resembles in its chemical properties the membranes of the lens and vitreous humor. These membranes consist of a mechanical mixture of a mucinoïd material with sparingly soluble, nitrogen-rich (14·77 per cent.) albuminoïd substance, which agrees in its properties neither with collagen nor

with elastin. Descemet's membrane is not digested by either gastric or pancreatic juice, but the lens capsule is completely dissolved. The solubilities of the lens capsule in other reagents are greater than those of Descemet's membrane. The main substance of the lens capsule is very like elastin.

The Vitreous Humor.—The fluid filtered off from the vitreous humor contains proteïd and mucin. Observers differ as to the variety of proteïd present, and also as to the presence or absence of mucin. It was found necessary to dilute the fluid very considerably before acetic acid caused a precipitate of mucin. This may account for the discrepancy. It is regarded as a mucoïd rather than as mucin proper; it contains 12·27 nitrogen and 1·19 sulphur per cent. The membranes of the vitreous yield gelatin.

Aqueous Humor.—This contains proteïd, but no mucin.

W. D. H.

Absence of Bile Acids, Hippuric acid, and Benzoic acid from the Suprarenal Capsules. By E. STADELMANN (*Zeit. physiol. Chem.*, **18**, 380—396).—Recent experiments on the functions of the suprarenal capsules render it necessary that exact knowledge should be obtained of their chemical composition. The present research shows that certain substances described by other authors in the glands, namely, bile acids, hippuric and benzoic acids, are not present.

W. D. H.

Proteïds of Milk. By M. ARTHUS (*Arch. de physiol.*, 1893, 673—677).—The experiments show that, in addition to caseïnogen, milk contains other proteïds. These differ from caseïnogen in being coagulable by heat, and, like Sebelien, the author separates them into lactalbumin and lactoglobulin.

W. D. H.

Alcalptonuria. By H. EMBDEN (*Zeit. physiol. Chem.*, **18**, 304—334; compare Abstr., 1893, ii, 82).—It has been abundantly shown since the publication of Wolkow and Baumann's researches on this subject (Abstr., 1891, 1128; 1892, 925), that the abnormal substance known as alcapton is homogentisic acid. References to published cases are given; in one of these glycosuria was present as well. The present paper relates to certain experiments on metabolism, performed with a view of testing the correctness of the hypothesis that the abnormal constituent of the urine originates by an unusual form of metabolism from tyrosine.

The first experiments were performed on the patient alluded to in the author's previous publication. It was found that the acid in the urine was increased by a flesh diet, that the administration of tyrosine doubled the excretion of the acid, that phenylacetic and phenylamido-acetic acids had no such influence, that oil of turpentine, kephir, and castor oil, although lessening the combined sulphates of the urine due to lessened putrefaction in the alimentary canal, had little or no influence on the amount of homogentisic acid. On administering the acid by the mouth, about 75 per cent. was excreted in the urine. Another point noted in the urine of this patient was an abnormally low excretion of uric acid (estimated by Fokker's method). The second series of experiments performed on healthy men and animals

showed that after the administration of the acid (by the mouth in man and by subcutaneous injection in dogs), the urine assumed all the characters of the urine of alcaptonuria, the amount of acid recovered in the urine being considerable, but nevertheless indicating that some had been destroyed in the living tissues.   W. D. H.

Rare Urinary Calculi. By J. HORBACZEWSKI (*Zeit. physiol. Chem.*, **18**, 335—340).—The first stone examined was a fatty concretion, and analysis gave the following result.

	Per cent.
Water	2·5
Ash	0·8
Organic matter insoluble in ether	11·7
Organic matter soluble in ether	85·0
Containing—	
Free fatty acids	51·5
Fats	33·5
Cholesterol	traces.

The organic matter insoluble in ether contained insoluble soaps of calcium and magnesium, and probably some blood proteïd and mucin.

The second stone was a cholesterol concretion. It contained—

	Per cent.
Water	3·76
Ash	0·55
Organic matter	95·99
Containing—	
Cholesterol	95·87
Organic matter insoluble in ether	0·15

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Cellulose in Bacilli and other Fungi. By I. DREYFUSS (*Zeit. physiol. Chem.*, **18**, 358—379).—The organisms investigated were *Polyporus, Agaricus campestris, Bacillus subtilis,* pus bacilli, and *Aspergillus glaucus.* It was found that all contain "true cellulose," in E. Schulze's sense. The presence of hemi-cellulose is very doubtful.

Cellulose was also found in caseating lymph glands, and thus an observation of Freund's is confirmed. It doubtless is due to the bacilli in the tuberculous deposits.   W. D. H.

Decomposition of Hydrogen Peroxide by Cells. By A. GOTT-STEIN (*Virchow's Archiv*, **133**, 295—307).—Liebreich was the first to

use hydrogen peroxide for distinguishing between living bacteria and those killed by heat, the former decomposing the peroxide, the latter not. This evolution of oxygen is here recommended as a macroscopic test for the presence of bacteria, for instance, in drinking water.

Many living cells act in the same way, so also do certain proteïds, such as fibrin, which are non-living.

The present experiments show that this power of the cells does not necessarily depend on the life of the cells; many vigorous antiseptics do not prevent it; certain substances, however, which are not antiseptics in the narrow sense do destroy the power; those particularly mentioned being hydrocyanic acid, chloral hydrate, and chloral cyanhydrin. Heating to 70° destroys the power. unless the cells are dried, when it has not this effect.

. It is further shown that nucleïn prepared from yeast, pus, liver, and other cells possesses the power of decomposing hydrogen peroxide. Negative results were, however, obtained with nucleic acid and artificial nucleïn, but the number of experiments in which these were used was small. The theory is advanced that cells, bacteria, and proteïds act in this way in virtue of the nucleïn they contain, and the process is regarded as a chemical rather than a catalytic phenomenon.

W. D. H.

Cause of Electric Currents observed in Plants. By O. HAACKE (*Ann. Agron.*, **19**, 396—399; from *Bot. Centr.*, **54**, 13).—According to Künckel, electric currents in plants are due to the movements of water in the tissues, and not to differences of potential, existing independently. The author considered it probable that vegetable electricity was due to biological processes, especially respiration and the consequent chemical changes. He experimented with leaves and flowers of dicotyledons and on a large mushroom in an atmosphere of hydrogen. The electric current was diminished, but never quite suppressed, owing, probably, to intramolecular respiration. On readmitting air, the electric current revives. Young bean plants behaved differently, the current being increased in an atmosphere of hydrogen. This is explained by the known fact that beans are distinguished by a very high intramolecular respiration.

Flowers, and especially stamens and pistils, show very decided oscillations under the influence of electric currents.

It is not possible to state exactly in what manner respiration gives rise to electric currents without a knowledge of the successive chemical changes which take place during respiration. The results of the author's experiments seem to indicate that vegetable electricity is not exclusively due to filtration of water. N. H. M.

Influence of Carbonic Oxide on Germination. By A. MARCACCI (*Chem. Centr.*, 1893, ii, 376; from *Arch. ital. Biol.*, **19**, 140).—Carbonic oxide, in a similar manner to chloroform and ether, prevents the germination of seeds, and retards the process of putrefaction and the growth of micro-organisms. E. C. R.

Mannitol and Dulcitol in the Vegetable Kingdom. By A. N. MONTEVERDE (*Ann. Agron.*, **19**, 444—446; from *Bot. Centr.*, Bei-

hefte **3**, 199).—Mannitol and dulcitol are true plastic substances in the case of *Rhinanthus, Euphrasia,* and *Melampyrum ;* they disappear when the plants are kept in the dark, and reappear under more favourable biological conditions; but they nourish only such plants as contain them normally. When *Rhinanthus* and *Euphrasia* are fed with glucose or cane sugar, mannitol is produced; *Melampyrum* similarly fed yields dulcitol. *Scrophularia nodosa,* contrary to what has been stated, contains neither one nor the other, and has not the power of transforming them into starch. *Euonymus europœus* contains much dulcitol at the budding period, but none in winter. The same holds (for mannitol) in the case of *Syringa vulgaris.* An examination of 797 species of *Scrophulariaceœ* showed that mannitol is present in 272 species, dulcitol in 26 species. It thus seems that the presence of one or the other of these carbohydrates is a constant character not only of an order, but also of a sub-order. Mannitol occurs in some *Orobanchaceœ,* in the *Oleaceœ* (A. Mayer) in celery and parsley. Some *Celastraceœ* contain dulcitol.   N. H. M.

Analytical Chemistry.

New Gas-volumeter of General Applicability. By F. GANTTER (*Zeit. anal. Chem.*, **32**, 553—564).—The principle of the method consists in the measurement of a liquid expelled by the evolved gas.
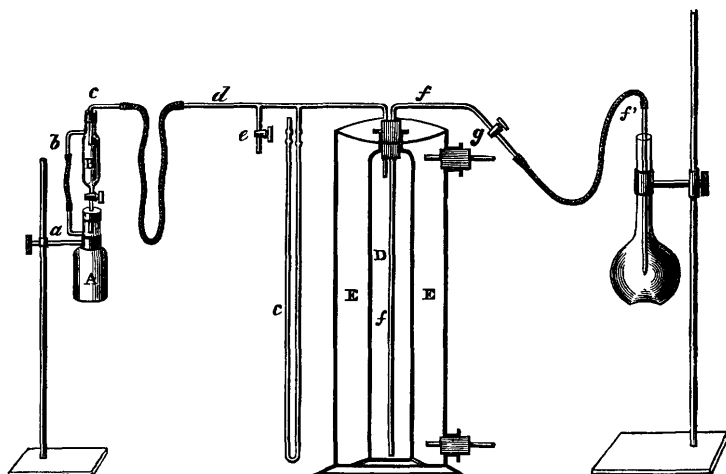
The cylinder D and tube *f* are filled to the point of *f′* with a liquid in which the gas to be liberated in not soluble : *g* is then closed. For carbonic anhydride, a solution of calcium chloride of sp. gr. 1·4 serves

well. The substance is weighed into A, and the reagent placed in B, and A and B are then plunged into the water-jacket E. When equilibrium of temperature is attained, pressure is equalised by opening e for a moment. The tube f' is now placed in an empty flask of known capacity, and g is opened. The gas is next evolved by allowing the reagent to flow into A, and the contents of A are boiled, the internal pressure being all the time maintained below that of the atmosphere by keeping the point of f' at a lower level than the surface of the liquid in D, but as soon as cooling commences f' must be raised so as to produce a small excess of internal pressure, and its point must be kept plunged in the liquid in the flask. The reaction vessels are again plunged into the water in E, and when cooling is complete f' is lowered until the manometer C shows that the pressure is the same as at the outset; g is then closed, f' removed from the flask, and the unoccupied portion of the flask measured by filling up to the mark from a burette. It is necessary that the temperature of E should be exactly the same at the end as at the beginning, and if it is desired to avoid reduction of the gas volume to normal temperature and pressure, an experiment with a pure substance will give in half an hour a factor for direct calculation from the observed volume under the existing conditions.

In estimating ammonia by decomposition with hypobromite, it is best to put the hypobromite in A, and the ammoniacal solution in B, and, finally, to rinse B thrice with the hypobromite by inclining the apparatus so that the liquid flows from A through a and b to B.

Nitric acid can also be estimated by decomposition with copper and sulphuric acid, but for this purpose a special laboratory vessel is required, from which the air can be expelled by hydrogen.

<div align="right">M. J. S.</div>

Borax as a Basis for Acidimetry. By T. SALZER (*Zeit. anal. Chem.*, **32**, 529—537; see Rimbach, Abstr., 1893, ii, 232).—The author suggested the use of borax as a standard alkali in 1857, but the impossibility of obtaining solutions of normal strength operated against its adoption at the time. It is, however, far preferable to work with weak solutions, since the tendency of boric acid to redden litmus disappears on dilution. Methyl-orange may be used as indicator in the titration of mineral acids, but in dilute solutions is far less sensitive than litmus: for organic acids it is inadmissible. The borax used must be free from octahedral crystals; it should lose 47·1 per cent. of water when ignited. A decinormal solution (19·0872 grams per litre) is of convenient strength, and acids must be diluted to a strength not exceeding N/10 before titration. The acid is to be coloured a pale yellowish-red with sensitive litmus tincture, and the borax solution run into it until the colour just changes to a bluish-red, and no longer returns to yellowish-red on stirring. Mineral acids, oxalic, acetic, and tartaric acids give satisfactory results; phosphoric acid behaves like a monobasic acid. These acids give practically the same results when the acid is run into the borax as when the process is reversed. Citric acid can equally well be titrated by the borax solution, but when the citric acid is run into the borax more acid is consumed, seemingly from formation of borocitric acid.   M. J. S.

Phenolphthaleïn as an Indicator. By R. T. THOMSON (*J. Soc. Chem. Ind.*, **12**, 432—433).—The author has found that boric acid may be accurately titrated with standard solution of sodium hydroxide, using phenolphthaleïn as indicator, but it is necessary to add to the liquid about one-third·of its bulk of glycerol.   The amount of boric acid contained in borax may be estimated in the same manner, after first adding sufficient sulphuric acid to combine with the soda, methyl-orange serving as indicator.   The excellent results obtained by the author are probably due to the greater viscosity of the liquid, caused by introducing the glycerol.   L. DE K.

Extraction of the Gases Dissolved in Water. By J. ROBSON (*J. Soc. Chem. Ind.*, **11**, 504).—The apparatus used is a modification of that of Kreusler for the estimation of nitric acid.   The gases are boiled out from the water in a flask from which the air has been com-pletely expelled by steam, and are collected in a vertical cylinder of 150 c.c. capacity, closed at its lower end by a cork, and at its upper end connected by a rubber tube to a Schiff's nitrogen measurer. Through the cork of this cylinder pass two tubes, the one connected to the long narrow neck of the extraction flask, and the other with a reservoir of boiling distilled water at a higher level.   A figure shows the arrangement of the apparatus and the mode of using it.

<div align="right">M. J. S.</div>

Estimation of Dissolved Oxygen. By G. ROMIJN (*Rec. Trav. Chim.*, **12**, 241—247).—The sample of water is taken from any required depth beneath the surface by means of a pipette of known volume.   The pipette is furnished with three-way stopcocks above and below, the upper stopcock having above it a small bulb with a fiducial mark on its free neck, and of known volume, about one-twentieth the capacity of the pipette.   The pipette is filled by the aid of a small pump, the liberation of dissolved gases from the water in the pipette, owing to reduction of pressure due to the action of the pump, is avoided by having the aperture of the lower stopcock of double the diameter of that next the bulb.   The upper three-way tap allows of the water sampled being drawn through the pipette in quantity sufficient to ensure the purity of the sample.

The pipette being full and the upper bulb empty, the lower tube is connected with a reservoir containing sodium hyposulphite (Na_2SO_2) solution, and a little of the solution is run through the stopcock to wash out the tube and tap ; the bulb is then placed in communication with the pipette, and, the lower cock being turned, hyposulphite solution is run in until the displaced water reaches the mark on the neck of the bulb ; the taps are now turned off at both ends of the pipette, and the whole set aside for about ten minutes.   The same volume of iodine solution is then introduced in the same manner, the lower tap and tube washed with water, the remaining contents of the pipette transferred to a flask, and the residual iodine determined by thiosulphate in the usual way.

The hyposulphite solution is kept in a bottle connected with a small hydrogen generator, arranged so as to keep an atmosphere of

hydrogen under pressure over the solution, the pressure being sufficient to force the solution into the pipette.

If V be the volume of the pipette, v the volume of the bulb between the mark and the upper tap, then the volume of water ultimately used for the titration is $(V - v)^2/V$.

Let O be the titre of oxygen, in cubic centimetres per litre of water, then $O = (A - B)a$. In this formula, A represents the number of cubic centimetres of thiosulphate used, B the number of cubic centimetres of thiosulphate which would be used for water free from oxygen, and a is a constant depending on the dimensions of the pipette and the titre of the thiosulphate solution.

B can best be determined by an experiment with water saturated with air at a known temperature, of which the oxygen titre is known from Roscoe and Lunt's or Winkler's determinations. The constant $a = \dfrac{8000}{1\cdot43} \cdot \dfrac{V}{(V - v)^2} \cdot r$. In this formula, $\dfrac{1000\,V}{(V - v)^2}$ is the factor for calculating from the volume of water used, the figure for a litre of water; $8/1\cdot43$ is the factor reducing the weight-equivalent of oxygen to the corresponding volume equivalent; and r is the factor used in reducing the actual volume of thiosulphate used to the equivalent volume of normal solution.

A correction is required if the water contains any substance such as hydrogen sulphide, which itself absorbs iodine, or when only about 2 c.c. of oxygen per litre is found and the deficiency is caused by a rapid decomposition of organic matter; this is found by a preliminary experiment to determine the iodine so absorbed.　　　　　W. T.

Detection of Iodic acid in Nitric acid. By E. PIESZCZECK (*Chem. Centr.*, 1893, ii, 337; from *Apoth. Zeit.*, **8**, 322).—The iodic acid is reduced with hydrogen sulphide, tin filings, or sulphurous anhydride. It is most convenient to use tin, in which case 10 c.c. of the acid is gently warmed with a few scraps of tin, and, after a few minutes, shaken with a small quantity of chloroform, which remains colourless in the absence of iodine or iodic acid.　　　　　E. C. R.

Influence of Ammonia on the Estimation of Hydrochloric acid in the Stomach Contents. By H. STRAUSS (*Chem. Centr.*, 1893, ii, 379—380; from *Berlin Klin. Woch.*, **30**, 398—402).—See this vol., ii, 21.

Estimation of Phosphorus in Steel and Iron containing Silicon. By J. SPÜLLER and S. KALMAN (*Zeit. anal. Chem.*, **32**, 538—550).—In the precipitation of phosphoric acid by molybdate from solutions containing silica, a certain quantity of a silicomolybdate is apt to separate. This precipitation is much favoured by the presence of ammonium salts, especially the nitrate; potassium nitrate is without influence. The lower the temperature at which the precipitation takes place, the smaller the amount of silicomolybdate formed, so that by proceeding in the following manner a correct determination can be made even in presence of silica. Of steel, 3·3 grams is dissolved in 50—55 c.c. of nitric acid (1·2 sp. gr.) in a $\frac{1}{4}$ litre conical

flask, at first in the cold, but finally with vigorous boiling. When all nitrous vapours are expelled, the solution is treated with 8 c.c. of a 3 per cent. solution of potassium permanganate, and boiled until the red colour disappears. The precipitated manganic oxide is reduced by adding 4 c.c. of a 10 per cent. solution of potassium nitrite, and, after cooling to 55—60°, the phosphoric acid is precipitated by adding 80 c.c. of molybdate, or, equally well, it may be cooled completely before adding the molybdate, and then warmed to 40°. The mixture is now kept for two hours at 36—40°, with an occasional shake ; the precipitate which forms is collected, and since it has a tendency to pass through the filter, this should be prepared by pouring upon it a thin pulp of paper fibres. The molybdate solution is made by dissolving 150 grams of ammonium molybdate to a litre, and pouring it into a litre of nitric acid (1·2 sp. gr.). The precipitates, after being washed, first with a mixture of 100 vols. of molybdate solution, 20 vols. of nitric acid, and 80 vols. of water, and then with a 10 per cent. solution of ammonium nitrate, are dissolved from the filter with a little dilute ammonia, and the solution evaporated and gently ignited in small porcelain basins until the ammonium salts are expelled.

Cast iron requires 60—80 c.c. of nitric acid to dissolve 3·3 grams, and should be very finely powdered. It usually contains so much phosphorus that only one-half to one-fifth of the solution need be precipitated, and if so much silica is present that part of it separates as a gelatinous precipitate, the solution should be made up to a known volume, and run through a filter before measuring out an aliquot part. .   M. J. S.

Estimation of Arsenic and Phosphorus in Iron Ores. By J. PATTINSON and H. S. PATTINSON (*J. Soc. Chem. Ind.*, **12**, 119—121). —The authors recommend treating 3 grams of the ore with hydrochloric acid. After rendering the silica insoluble by evaporation, the residue is taken up with a very little acid, and then diluted with hot water to 50 c.c. A 50 per cent. solution of sodium thiosulphate is now run in until the iron is completely reduced to the ferrous state. The sulphurous acid is expelled by boiling, and, after cooling, 5 c.c. of strong hydrochloric acid is added. A little powdered zinc sulphide is now introduced, which causes the precipitation of any arsenic as trisulphide. The precipitate is first washed with hot 5 per cent. hydrochloric acid to remove any lead, and, after washing with water, it is digested with ammonium sulphide. The solution is evaporated to dryness on the water bath, the residue oxidised with bromine and a little nitric acid, and the arsenic finally precipitated, and weighed, as magnesium ammonium arsenate. The filtrate from the arsenic trisulphide is boiled to expel hydrogen sulphide, and diluted to 250 c.c. ; a little ferric chloride is added, and the liquid neutralised with calcium carbonate. This will cause a precipitate of ferric phosphate, which must be washed on a filter with lukewarm water. To estimate the phosphorus, it must be dissolved in dilute nitric acid, and heated with solution of ammonium molybdate ; this causes the precipitation of ammonium phosphomolybdate, which is then collected and weighed. The test analyses are certainly extremely satisfactory,

but, as no silicates were introduced, no evaporation to dryness in presence of hydrochloric acid was required, and therefore there could be no loss of arsenic. L. DE K.

Estimation of Boric acid in Boronatrocalcite. By G. A. LE ROY (*Chem. Centr.*, 1893, ii, 291; from *Bull Soc. ind. Rouen*, **21**, 62).—2·5—5 grams of the finely-powdered substance is decomposed in a reflux apparatus with a few c.c. of sulphuric acid diluted with an equal volume of water. The presence of a small quantity of hydrochloric acid facilitates the decomposition. The cooled mixture is filtered, the filter washed with acidified water, the filtrate neutralised with soda, heated to boiling, and again filtered. The filtrate is acidified with hydrochloric acid, boiled to expel carbonic anhydride, and then made up to a known bulk with water free from carbonic acid. The solution contains free boric acid and alkali sulphate and chloride.

20 c.c. of the solution is placed by the side of the same bulk of water, and an equal number of drops of a 10 per cent. solution of Poirrier's Orange III added to each. The acid solution is then titrated with a solution of sodium hydroxide until it acquires the same colour as the aqueous solution of the indicator. This titration gives the quantity of free hydrochloric acid. A second 20 c.c. of the acid solution is titrated with sodium hydroxide in the presence of Orange II until it acquires a dark-red colour. The difference in the two titrations gives the quantity of boric acid. The sodium hydroxide must be free from carbonates, silicates, and aluminates.

E. C. R.

Analysis of Silicon Carbide. By O. MÜHLHAEUSER (*Zeit anal. Chem.*, **32**, 564—567).—The analysis of this substance, which is being produced in America as a substitute for emery and bort under the name "Carborundum," presents peculiar difficulties, in consequence of its extreme hardness. After trituration in an agate mortar, it is necessary to submit the powder to elutriation, and accurate results in the carbon determination can only be obtained with that which remains in suspension for at least five minutes. The carbon is best estimated by combustion with 20 parts of lead chromate (the addition of potassium dichromate causing the oxidation to proceed with explosive rapidity); the silicon by fusion with potassium sodium carbonate for about six hours, during which the heat should be raised very gradually. A very pure specimen gave the following numbers:— C 30·2, Si 69·1 (Al, Fe)$_2$O$_3$ 0·46, CaO 0·15, MgO 0·09 per cent. The formula SiC requires 30 per cent. of carbon. M. J. S.

Estimation of Copper as Cuprous Sulphide. By R. WEG-SCHEIDER (*Monatsh.*, **14**, 315—322).—The author has found that in order to obtain accurate results in estimating copper as cuprous sulphide by heating the precipitated cupric sulphide in a current of hydrogen, the temperature must not be allowed to rise too high. A temperature of about 650° (dull red heat) is the highest which can be safely employed, as at higher temperatures than this a portion of the sulphide is reduced to metallic copper, hydrogen sulphide

being evolved. The substitution of coal-gas for hydrogen does not give good results. When hydrogen sulphide is employed instead of hydrogen, a portion of the cupric sulphide remains unreduced.

A. H.

Separation of Metals in Alkaline Solution by means of Hydrogen Peroxide. By P. JANNASCH (*Ber.*, **26**, 2329—2331; compare Abstr., 1893, ii, 492).—Copper peroxide is precipitated on adding hydrogen peroxide to a solution of cupric hydroxide in dilute ammonia, but the reaction does not occur in presence of even slight excess of ammonia or ammonium salts. The precipitation is, in any case, incomplete, 1·5—2 per cent. of copper remaining dissolved. Copper peroxide forms voluminous, dark olive-green flocks, and appears to attack porcelain, as it was always found to contain silica. It is possible, by the help of hydrogen peroxide, to show in one solution the various oxidation stages of copper. On mixing 10 per cent. copper sulphate solution (3 c.c.) with 20 per cent. soda (4 c.c.), cupric hydroxide is precipitated; this is dissolved in 10 per cent. tartaric acid (3 c.c.) and 2 per cent. hydrogen peroxide solution (15 c.c.) added; copper peroxide is precipitated, but dissolves on heating, and on cooling the solution, cuprous oxide is deposited.

J. B. T.

Separation of Metals in Alkaline Solution by means of Hydrogen Peroxide. By P. JANNASCH and J. LESINSKY (*Ber.*, **26**, 2331—2334, 2334—2336; compare preceding abstract).—*Separation of Lead from Copper.*—Lead nitrate (0·5 gram) and copper (0·3 gram) are dissolved in water (50 c.c.) and concentrated nitric acid (10 c.c.), and the solution treated at ordinary temperatures with a mixture (80—125 c.c.) of 3 parts of hydrogen peroxide (2 per cent.) and 1 part of strong ammonia. Saturated solution of ammonium carbonate (5 c.c.) is added, and the precipitate is washed 4 or 5 times with a mixture of hydrogen peroxide (1 part), concentrated ammonia (1 part), and water (6—8 parts); when all the copper is separated, the washing is continued with dilute ammonia (1 : 8) at 60—80°, and finally with warm water, in which the lead hydroxide is completely insoluble. The lead precipitate is dried and treated in the manner previously described (Abstr., 1893, ii, 493). The copper in the filtrate is determined in the usual manner, with due regard to the presence in the solution of nitric acid and ammonium salts. A large excess of hydrogen peroxide causes the lead to be precipitated in dense, crystalline plates. Mixtures of lead nitrate and copper sulphate may be separated in a similar manner if the precipitation of lead sulphate is prevented by the addition of acetic acid and ammonia. The analytical results agree closely with the theoretical.

Separation of Lead from Zinc.—Lead nitrate (0·5 gram) and zinc oxide (0·2 gram) are dissolved in concentrated nitric acid (2 c.c.) and water (50 c.c.); the solution is treated with a mixture of 2—3 per cent. hydrogen peroxide (40 c.c.) and concentrated ammonia (15 c.c.); saturated ammonium carbonate solution (5 c.c.) is then added, and the liquid well stirred, the lead oxide is collected, washed first with dilute ammonia and finally with cold water, and treated in the manner already described (*loc. cit.*). The concentrated filtrate

is treated with pure sodium hydroxide (5 grams) and boiled until free from ammonia; it is then acidified with hydrochloric acid, and the zinc precipitated with sodium carbonate and determined in the usual manner, care being taken to free it from silica or alumina. The lead oxide may also be precipitated in the crystalline form (see above).

Separation of Lead from Nickel.—Lead nitrate (0·5 gram) and potassium nickel sulphate (0·4 gram) are dissolved in concentrated nitric acid (5 c.c.) and water (50 c.c.), glacial acetic acid (5 c.c.) and strong ammonia (15 c.c.) are then added, and the lead precipitated with a mixture of hydrogen peroxide (75 c c.) and concentrated ammonia (20 c.c.); the addition of ammonium carbonate is unnecessary. The lead oxide is precipitated in a flocculent condition, and is treated in the manner described in the separation of lead from copper (see above). The solution containing the nickel is evaporated to dryness, treated with concentrated hydrochloric acid (15 c.c.), evaporated to dryness again, the residue dissolved in dilute hydrochloric acid, the silica separated; the filtrate (250—300 c.c.) is then boiled, treated with aqueous hydroxylamine hydrochloride (4 grams), and precipitated with 15 per cent. soda (60—70 c.c.) in the usual manner. Hydroxylamine, in contradistinction to ammonia, causes the nickel to be precipitated in a form which admits of rapid filtration. The numerical results show a tolerably close agreement with the theoretical. J. B. T.

Estimation of Manganese by means of Potassium Permanganate. By A. GORGEU (*Bull. Soc. Chim.*, [3], **9**, 490—496).—When manganese is estimated, as in Guyard's method, by adding a solution of potassium permanganate to an almost neutral solution of manganous chloride, heated at 80°, the results are too low, partly in consequence of the acidity of the liquid. Donath's modification, in which the solution of the manganous salt is added to a solution of the permanganate mixed with sodium carbonate, also gives inexact results, unless the solutions are mixed very slowly, especially towards the end of the reaction. If Guyard's process is modified by adding precipitated calcium carbonate before the permanganate, the results are less exact than by Donath's method.

According to Guyard, three manganese permanganates, Mn_5O_{10}, Mn_6O_{11}, and Mn_7O_{12}, can be obtained by mixing potassium permanganate and manganous chloride in different proportions. He seems, however, to have overlooked the fact that hydrogen chloride is liberated at the same time. The author finds that the oxide Mn_7O_{12} is never formed, even when the liquid is kept neutral, and the two oxides Mn_6O_{11} and Mn_5O_{10} are only formed when the acid that is set free is continually neutralised with calcium carbonate. The author criticises Guyard's views as to the constitution of these oxides, and contends that there is no evidence that they are manganese permanganates, and also that Guyard has advanced no evidence of the existence of manganese manganates. C. H. B.

Estimation of Oxide of Iron and Alumina in Mineral Phosphates. By A. SMETHAM (*J. Soc. Chem. Ind.*, **12**, 112—116).—The author uses Glaser's process, and checks the results by his ammonium acetate method. The analyses should agree within 0·1 per cent. The ammonium acetate process is carried out as follows :—2 grams of the sample is evaporated with strong hydrochloric acid, and the residue is taken up with 10 c.c. of dilute acid, and filtered from any siliceous residues. After boiling with a few drops of bromine, the liquid is allowed to cool, and mixed with dilute ammonia until a permanent precipitate is produced, which is then again dissolved by cautious addition of hydrochloric acid. Large excess of ammonium acetate is now added, and the precipitate is collected on a filter, well washed, burnt, and weighed. It theoretically consists of ferric and aluminium phosphates, but in practice it will be found to contain variable quantities of calcium phosphate. It must, therefore, be quantitatively tested for phosphoric anhydride, calcium oxide, and ferric oxide ; the alumina. then being found by difference. The author conducts the analysis as follows :—The precipitate is dissolved in hydrochloric acid, diluted with water, and, after adding some citric acid, boiled with ammonium oxalate. Dilute ammonia is then added until the liquid is neutral to litmus paper, and subsequently acetic acid to slightly acid reaction. The calcium oxalate is collected after some time, and ignited to carbonate as usual. The filtrate from the lime is mixed with magnesia mixture, the precipitate being afterwards purified by redissolving and reprecipitating, and from the filtrate from the magnesium ammonium phosphate, the iron is precipitated with ammonium sulphide and treated as usual. The calcium carbonate is calculated to oxide ; the magnesium pyrophosphate to phosphoric anhydride ; to their sum is added the weight of the ferric oxide, and the deficiency represents the alumina.   L. DE K.

Electrolytic Estimations and Separations. By G. VORTMANN (*Monatsh.*, **14**, 536—552).—The author describes the behaviour on electrolysis of salts of zinc, iron, cobalt, and nickel, to which solutions of an alkaline tartrate and an alkaline hydroxide have been previously added. Of these metals, the three first named may be quantitatively deposited from the alkaline solution ; whilst, under the same conditions, the last named remains in solution, thus affording a method for the separation of nickel from zinc, iron, and cobalt. Iron may be separated from zinc in alkaline tartrate solution by employing a cathode of platinum, whereby the iron is deposited with only a trace of zinc. By dissolving and redepositing two or three times, the iron is obtained entirely free from zinc. To estimate zinc in presence of iron, potassium cyanide is first added to the solution, whereby the iron is converted into potassium ferrocyanide ; sodium hydroxide is then added and the current passed, when the zinc is deposited, the iron remaining in solution.

The author further describes a method of estimating cobalt, nickel, and copper when present with much iron. A solution of the metal , in which the iron is present as a ferric salt, is placed in a platinum dish and treated with excess of ammonia, and the current passed, where-

upon, without the necessity of filtering off the ferric hydroxide, cobalt. nickel, and copper are thrown down on the cathode in a well-adhering mass. In the separation of copper and iron, the latter metal is best oxidised with nitric acid. G. T. M.

Separation of Nickel from Cobalt. By H. HERRENSCHMIDT and E. CAPELLE (*Zeit. anal. Chem.*, **32**, 607—610; from *Le Cobalt et le Nickel*, Rouen, 1888).—The potassium nitrite process is not capable of giving a complete separation. Traces of nickel can be detected in presence of much cobalt by microscopic examination, in consequence of the different colours of cobaltic and nickelic hydroxides, that of cobalt being a pale brown, whilst nickelic hydroxide is black. On examining, with a magnifying power of 180 to 200 diameters, the precipitate thrown down by excess of sodium hypochlorite from the nearly neutralised solution, a completely black field will be seen if the nickel amounts to 1 per cent. of the cobalt, but when only traces are present, they are exhibited as black spots on a brown field. Traces of cobalt can be separated from much nickel by suspending the hydroxides in water or an alkali, and passing chlorine, when the nickel dissolves completely, the cobalt remaining undissolved. The practical method of estimating the two metals in ores, &c., is, therefore, as follows :—After removal of the metals precipitable by hydrogen sulphide and ammonium carbonate, an excess of ammonium sulphide is added, then a small excess of acetic acid, and the liquid is boiled. The precipitate is rapidly filtered off, and washed with hot ammonium acetate. It is then dissolved in nitric acid, the solution evaporated to dryness, taken up with water, filtered from sulphur, and divided into two parts. One part is evaporated with sulphuric acid, ignited very gently, and the residue of metallic sulphates weighed. The other half is treated with potassium cyanide and bromine, and the well-washed precipitate treated with chlorine. The solution containing the nickel is feebly acidified with hydrochloric acid, boiled to expel chlorine, and poured into boiling soda. The precipitate is washed, dissolved in hydrochloric acid, and converted into sulphate, as above, for weighing. When zinc is present, the mixed sulphates of nickel and zinc are dissolved, and the metals precipitated by hydrogen sulphide, after adding ammonium acetate and acetic acid. The precipitate is treated with dilute hydrochloric acid, potassium cyanide added to the neutralised solution, and the zinc thrown down by potassium sulphide and weighed. The corresponding quantity of sulphate is deducted from the weight of the mixed sulphates.

M. J. S.

Estimation of Chromium in Ferrochromium and Steel. By J. CLARK (*J. Soc. Chem. Ind.*, **11**, 501—504; **12**, 340—341).—Finely pulverised ferrochromium, if rich in chromium, is very readily oxidised when heated with a mixture of magnesia and sodium hydroxide (2 parts of the former to 3 of the latter). The crucible containing the intimate mixture is heated for half an hour with the tip of a small bunsen burner flame, and subsequently for another half hour to dull redness. The contents are then boiled with water, hydrogen

peroxide is added to reduce any manganate, and, after boiling for some minutes, the solution is filtered. The insoluble matter may still contain chromium. It should be ignited, ground in an agate mortar, and again fused with the magnesia-soda mixture, and this fusion may even need to be repeated a third time. The solutions are acidified with sulphuric acid, and the chromic acid titrated by Penny's process. For poor alloys, ignition in a porcelain crucible over the blowpipe or in a muffle with 3 parts of calcium hydroxide should precede the ignition with magnesia-soda mixture. In this case about 3 parts of sodium hydrogen carbonate should be added to the solution before filtration, for the purpose of removing the calcium. Second and third fusions are required in this method also. The powdered ferro-chromium may also be prepared for the fusion with magnesia-soda by a preliminary heating in sulphur vapour, or, better, vapour of carbon bisulphide, in a boat in a porcelain tube. The sulphides produced are very bulky, and, in the case of sulphur, a slight loss results from the violence of the action. The sulphides may be at once mixed with 8 parts of magnesia-soda, or be first roasted in a porcelain crucible, and then fused with 5 parts of the mixture.

Chromium steel is best attacked by the carbon bisulphide method. The residue from the first fusion with magnesia-soda will usually yield a very small amount of chromate on a second fusion. In cases where the alloy can be dissolved in dilute hydrochloric acid, the solution is treated with ammonia until a permanent precipitate is produced, and then with a small excess of sodium phosphate and about double that amount of sodium thiosulphate or, preferably, sulphite, and boiled for 10 minutes. The precipitate, which contains all the chromium, is washed, gently ignited, ground, and fused with 8 parts of magnesia-soda. Equally good results are obtained when the hydrochloric acid solution is neutralised with sodium carbonate, and boiled with sodium sulphite as long as sulphurous anhydride comes off. The precipitate, which contains all the chromium as basic sulphite, is ignited and fused as above.   M. J. S.

Estimation of Cyanides in Gas Refuse. By W. LEYBOLD (*Zeit. anal. Chem.*, **32**, 571—572).—The powdered substance is treated with soda to convert the cyanide into ferrocyanide, and a portion of the solution is evaporated to dryness with excess of sulphuric acid, and heated until the excess of acid is expelled. The ferric sulphate which remains is dissolved in sulphuric acid, reduced with zinc, and titrated with permanganate.

A possible objection that, in the presence of organic matter, iron might be dissolved by the alkali in other forms than as ferrocyanide, is met by the consideration that there is always formed at the same time an alkaline sulphide, by which such iron would be precipitated.
                                                            M. J S.

General and Physical Chemistry.

Refractive Indices of Liquid Nitrogen and of Air. By G. D. LIVEING and J. DEWAR (*Phil. Mag.*, [5], **36**, 328—331).—The authors have determined the refractive indices of liquid nitrogen and air, using Terquem and Trannin's method of suspending in the liquid two parallel glass plates with a thin layer of air between them, and measuring the angle of incidence at which the ray suffers total reflection at the surface of the air. The liquid nitrogen was contained in a vacuum-jacketed tube, the liquid acting as a lens, and the source of light and the spectroscope-slit being conjugate foci when the liquid was midway between them. The glass plates were separated by a ring of thin filter-paper, thoroughly wetted with white of egg, and allowed to dry, and were attached to a rod which formed the prolongation of the vertical axis of a theodolite used to measure the angle through which they were turned.

The apparatus gave for liquid oxygen, $\mu_D = 1\cdot226$, slightly larger than the value obtained by the authors with a prism, namely, $1\cdot2236$.

For nitrogen which contained 5 per cent. of oxygen, the refractive index was found to be $\mu_D = 1\cdot2053$ at $-190°$, and for air, $\mu_D = 1\cdot2062$.

The refraction constant for liquid nitrogen, according to Gladstone's formula, is $0\cdot225$, and the refraction equivalent, $3\cdot153$; according to Lorenz's formula, these values become $0\cdot1474$ and $2\cdot063$ respectively.
J. W.

Polarisation of Platinum Electrodes in Sulphuric acid. By J. B. HENDERSON (*Proc. Roy. Soc.*, **54**, 77—82).—Of two platinum electrodes immersed in sulphuric acid and connected with the primary circuit, one was also connected with the earth, and the other through a key with one pair of quadrants of an electrometer. Connected with the same pair of quadrants, through another key, was the slider on a bridge with a special battery. The other pair of quadrants and one end of the bridge were earthed. The slider was so moved that the permanent deflection it gave on the electrometer was not disturbed when the primary circuit was broken and the polarised electrodes connected with the instrument. The potential of the quadrants was then that of the polarisation. The mean value of the electromotive force of polarisation determined in this way was $2\cdot09$ volts, the primary current varying from $0\cdot2$ to $1\cdot0$ amp., the time of its passing from 25 minutes to 18 hours, and the strength of the solutions from 5 to 30 per cent. The extreme values were $2\cdot05$ and $2\cdot14$.
J. W.

Use of Cupric Nitrate in the Voltameter and the Electrochemical Equivalent of Copper. By F. E. BEACH (*Amer. J. Sci.*, [3], **46**, 81—88).—The object of this paper is to show that cupric nitrate has some marked advantages over the sulphate for use in the voltameter. The nitrate solution freshly prepared has a tendency to dissolve copper, which decreases, however, after the copper

electrode has been kept in the solution for a sufficient length of time. Another difficulty is due to oxidation of the copper deposited, which may be prevented by the addition of a small amount of ammonium chloride. The following method is recommended for the preparation of the solution:—Dissolve copper nitrate, the purest obtainable, in distilled water. Boil for a short time to expel the air, and keep at a temperature of 100° for an hour or two in the presence of bright metallic copper in order to completely neutralise the solution. When ready for use, it should have a density of about 1·53. Add a saturated solution of ammonium chloride at about the rate of 1 drop to 100 c.c. of the nitrate. It is not easy to specify the proper amount of ammonium chloride necessary, and the surest way is to try a preliminary experiment. If too much be present, the deposit will discolour on drying; if too little, the deposit will oxidise in the solution. The weight of copper deposited does not appear to depend on the current density, and is practically independent of the temperature between 10° and 35°.

The equivalent obtained for copper, using the nitrate, agrees very well with that calculated from the best chemical determinations.

H. C

Ratio of the Specific Heats of Paraffins, &c. By J. W. CAPSTICK (*Proc. Roy. Soc.*, **54**, 101—104).—The ratio of the specific heats at constant volume and constant pressure of several gaseous paraffins and their halogen derivatives at the ordinary temperature was calculated from the velocity of sound in the gases obtained by using Kundt's method. The mean values of the ratio are as follows:—Methane, 1·313; methylic chloride, 1·279; methylic bromide, 1·274; methylic iodide, 1·286. Ethane, 1·182; ethylic chloride, 1·187; ethylic bromide, 1·188. Propane, 1·130; propylic chloride, 1·126; isopropylic chloride, 1·127; isopropylic bromide, 1·131.

It will be noticed that these ratios fall into four groups: (*a*) methane, (*b*) methylic haloïds, (*c*) ethane and its derivatives, (*d*) propane and its derivatives, the ratio for each group being constant.

A form of vapour density apparatus, giving results concordant to 0·1 per cent., is described in the paper.   J. W.

Thermal Properties of a Mixture of Carbonic Anhydride and Nitrogen. By K. TSURUTA (*Phil. Mag.*, [5], **36**, 438—453).—The author has calculated from Andrews' observations the isothermals, isometrics, and isopiestics of a mixture of carbonic anhydride and nitrogen in the proportion of 3 to 4. He uses Clausius' equation

$$p = \frac{RT}{v - \alpha} - \frac{K}{T(v + \beta)^2},$$ adopting Margules' values for the constants

R, K, α, β. The results are given in tabular and curve form.

J. W.

Dissociation Pressure and the Individuality of Chemical Compounds. By V. KURILOFF (*J. Russ. Chem. Soc.*, **25**, 170—192). —The author has studied the variation of the vapour pressure of ammonia with varying concentration in the liquid first obtained by Divers by passing ammonia over ammonium nitrate. The liquid behaves as if it were a solution of ammonium nitrate in ammonia,

the vapour pressure decreasing as ammonia is removed, until the solid begins to separate out, after which it remains constant, until the whole has become solid. The solubility of the ammonium nitrate in ammonia increases with rise of temperature.

Similar experiments were made with the liquid obtained by passing ammonia over ammonium bromide. The solution in this case seems to be one of the compound NH_4Br,NH_3 in ammonia. So long as solid and liquid are present together, the vapour pressure again remains constant.

Care must be taken, therefore, in drawing conclusions as to the individuality of substances from the constancy of their vapour pressure. This constancy may be due to the existence of an individual compound, but it may also arise from the presence of a heterogeneous mixed system. J. W.

Supersaturated Solutions. By A. L. POTILITZIN (*J. Russ. Chem. Soc.*, **25**, 201—207).—The author has stated (Abstr., 1893, ii, 509) that salts containing water of crystallisation which do not decompose at the ordinary temperature in dry air or in a vacuum, or decompose only very slowly, are incapable at that temperature of forming supersaturated solutions. The hydrated salt $CaSO_4,2H_2O$ is apparently an exception to this rule, as it does not lose water at the ordinary temperature, and still can give supersaturated solutions. This the author explains by assuming that the hydrate $2CaSO_4,H_2O$, which is more soluble than the hydrate $CaSO_4,2H_2O$, exists in the solution at the ordinary temperature, and only changes slowly into the dihydrate. J. W.

Distillation in a Vacuum. By A. ANGELI (*Gazzetta*, **23**, ii, 104). —In the distillation of small quantities of liquid under diminished pressure, very good results are obtained by almost filling the distillation flask with glass wool. W. J. P.

Inorganic Chemistry.

True Atomic Weight of Hydrogen. By G. HINRICHS (*Compt. rend.*, **117**, 663—666).—The author has applied his method of limits (Abstr., 1893, ii, 316) to the results of Keiser, Cooke and Richards, Dittmar and Henderson, and Morley, making use of some hitherto unpublished data supplied by the last. The application is somewhat difficult, because in each series of experiments the weight of materials employed has varied but little. It is clear, however, that the divergencies from the value $H = 1$ are functions of the weight of hydrogen employed, and if equal weight is attached to the work of Dittmar, Keiser, and Morley, the divergencies from this value fall on a curve which is represented by the formula $\eta = \dfrac{h}{5000}\,(5^2 - h^2)$, where h is the weight of hydrogen and η the divergence from unity.

5—2

For the limit $h = 0$, $\eta = 0$, and hence $H = 1$ exactly when $O = 16$ (compare *loc. cit.*).   C. H. B.

Relation between the Precipitation of Chlorides by Hydrochloric acid and the Reduction of the Freezing Point. By R. ENGEL (*Compt. rend.*, **117**, 485—488).—The law that 1 mol. of hydrochloric acid will precipitate from its saturated solution at 0° 1 atom of chlorine in the form of the chloride of a univalent or bivalent metal holds good for temperatures as high as 75°.

The law also holds good for the double chloride $CuCl_2,2NH_4Cl$, 1 mol. of which is precipitated by 4 mols. of hydrochloric acid.

Van't Hoff has shown that the molecular osmotic pressure of hydrochloric acid, 1·98, is practically the same as that of sodium chloride, 1·89, and therefore 1 mol. of the acid should precipitate 1·05 mol. of the salt. In the case of the chlorides of bivalent metals, the molecular reduction of the freezing point is not double that of the chlorides of univalent metals. The author finds, however, that the molecular reduction produced by chlorides of univalent metals remains practically the same for various concentrations, and for different chlorides varies only between 35 and 40. With chlorides of bivalent metals, on the contrary, the molecular reduction increases with the concentration and becomes practically double that of the univalent chlorides. The molecular reduction of the double salt $CuCl_2,2NH_4Cl$ also increases with the concentration and tends to become four times as great as that of univalent chlorides. The following table shows the relation between the nature of the chloride, the molecular reduction of the freezing point, and the number of molecules of hydrochloric acid required to precipitate 1 mol. of the salt.

	Atoms of chlorine in the molecule.	Ratio of the molecular reductions.	Mols. HCl.
Chlorides of univalent metals ..	1	1	1
,, bivalent ,, ..	2	2	2
Double chloride, $CuCl_2,2NH_4Cl$..	4	4	4

In this connection, it is important to observe, however, that sodium hydroxide, which has practically the same molecular osmotic pressure as hydrochloric acid, precipitates only $\frac{1}{2}$ mol. of sodium chloride, bromide, or iodide from a saturated solution.

When the number of molecules of water in combination with a molecule of a chloride at the freezing point of its saturated solution is calculated, it appears that the product of this number into the reduction of temperature is a constant which has double the value in the case of chlorides of bivalent metals that it has in the case of chlorides of univalent metals.

	Molecules of water.	Freezing point.	Product.
Ammonium chloride......	12·4	15·5	19·2
Potassium chloride.......	16·6	11·4	18·9
Potassium iodide	8·5	22·0	18·7

	Molecules of water.	Freezing point.	Product.
Sodium bromide.........	8·1	24·0	19·4
Ammonium iodide	6·4	27·5	17·6
Strontium chloride.......	22·9	17·0	38·9
Calcium chloride	10·7	37·0	39·6

C. H. B.

Ozone. By A. Wolkowicz (*Zeit. anorg. Chem.*, **5**, 264—265).— From a consideration of the position of oxygen in the periodic system, it is concluded that ozone has the constitution O:O:O, just as sulphurous anhydride is O:S:O. Ozone would then be the anhydride of an acid H_2O_4, corresponding with H_2SO_3. This acid, like sulphurous acid, is unknown, but potassium tetroxide, K_2O_4, is its potassium salt, and resembles the sulphite in its property of reducing permanganate. C. F. B.

Decomposition of Nitrous acid in Nitric acid Solution. By B. Liljensztern and L. Marchlewski (*Zeit. anorg. Chem.*, **5**, 288—292). —By passing a stream of carbonic anhydride through 60 per cent. nitric acid to which 4 per cent. of nitric peroxide had been added, and determining the ratio of nitrous to total nitrogen in the gases carried over, it was shown that the nitric acid contained nitrous acid in addition to nitric peroxide. Montemartini's statement (*Real. Accad. Linc.*, **1**, 63), that the reaction $HNO_2 + HNO_3 = 2NO_2 + H_2O$ is the only one that takes place in nitric acid of over 30 per cent. strength, is, therefore, erroneous. C. F. B.

Conversion of Yellow Phosphorus into Red Phosphorus. By J. W. Retgers (*Zeit. anorg. Chem.*, **5**, 211—230; compare Pedler, Trans., 1890, 599; Retgers, Abstr., 1893, ii, 457; Muthmann, *ibid.*, 458).—It is generally admitted that yellow phosphorus crystallises from the usual organic solvents in dodecahedra; the crystals are best obtained by cooling a hot solution. The author cannot substantiate the text-book statement that yellow phosphorus crystallises from essential oils in octahedra. Thus, whilst it is admitted that yellow phosphorus is crystalline, this substance has, on several occasions, been described as amorphous. This is not surprising in view of the fact that a thin layer of yellow phosphorus between two thin glasses has all the appearance of an amorphous substance.

When phosphorus is heated, it passes through three stages:—(1) it becomes yellow to brown, but remains transparent and regular; (2) a granular, undoubtedly crystalline, segregation occurs (formation of red, opaque phosphorus); (3) a graphitic, chocolate-coloured phosphorus is produced. The second stage corresponds with the first production of a true modification.

The same series of changes is produced by light—not merely superficially, as stated in text-books—a fact which the author calls in evidence of his contention that red phosphorus is not amorphous.

The author has not been able to determine the character of the white crust which forms on phosphorus which has been submerged

in water, but he inclines towards the opinion that it is a hydrate rather than a modification.

It is pointed out that the properties of an amorphous modification are never intermediate between those of two crystalline modifications. If red phosphorus were amorphous, this rule would be violated; for the specific gravity of red phosphorus is 2·148, whilst that of regular, yellow phosphorus is 1·826, and that of chocolate-coloured, hexagonal phosphorus is 2·34.

Some remarks in reply to Muthmann (Abstr., 1893, ii, 458) are included in the paper.   A. G. B.

Volatility of Pyrophosphoric acid. By G. WATSON (*Chem. News*, **68**, 199—200).—The author has made a series of experiments, heating weighed quantities of orthophosphoric acid for various periods, at fixed temperatures, and examining the products; from which he concludes that orthophosphoric acid requires a temperature above 230—235° for its complete dehydration into pyrophosphoric acid; that at 255—260° it is completely converted into pyrophosphoric acid, which is, moreover, volatile at that temperature; that at 290—300° metaphosphoric acid is beginning to form.   D. A. L.

Action of the Electric Arc on the Diamond, Amorphous Boron, and Crystallised Silicon. By H. MOISSAN (*Compt. rend.*, **117**, 423—425).—In the electric arc, at a somewhat high temperature, the diamond becomes incandescent, swells up without melting, and becomes covered with black masses, consisting entirely of hexagonal lamellæ of graphite, which is easily converted into graphitic oxide. If the diamond is placed in a small carbon crucible in the electric furnace previously described, and is subjected to the action of an arc produced by a current of 70 volts and 400 ampères, the crystal first breaks up into small fragments along the planes of cleavage, and then at a higher temperature swells up and is completely converted into graphite, which yields yellow graphitic oxide.   It follows that at the temperature of even a moderately intense electric arc, the stable form of carbon is graphite.   When heated in a carbon envelope at the temperature of the oxy-hydrogen blow-pipe, the diamond is sometimes covered with an adherent black mass, which slowly dissolves in a mixture of potassium chlorate and nitric acid, but which is not graphite.

Amorphous boron, prepared by means of magnesium, volatilises without fusion in the electric arc, the extremities of the electrodes being converted into partially-crystallised boron carbide.

Crystallised silicon, when heated in the arc, first melts and then boils, the extremities of the electrodes at the end of the experiment being covered with pale green crystals of carbon silicide.

The phenomena in the arc were observed by projecting on a screen by means of an intense arc an image of the arc of lower intensity in which the substances were heated.   C. H. B.

Silicon Carbide. By O. MÜHLHAEUSER (*Zeit. anorg. Chem.*, **5**, 105—125).—A mixture of finely-powdered coke, sand, and salt was

packed around a carbon core in an oblong fire-brick box. The core was connected with the terminals of a transformer, whereby it could be heated until the mixture surrounding it became white hot. A transverse section of the mass after the reaction showed that the core was surrounded by (*a*) a zone of adhering graphite, (*b*) a zone of crystalline silicon carbide, (*c*) a zone of amorphous silicon carbide, (*d*) a zone containing pockets of fibrous material, (*e*) a zone of the original mixture only slightly altered, and (*f*) a hard skin consisting almost entirely of salt.

The graphite has all the properties of the natural mineral, and the same crystalline form as that of the silicon carbide, a fact which indicates that the latter compound is at first formed in this zone and subsequently loses its silicon by volatilisation. The outer portion of this zone, when washed, left 33·71 per cent. of variously-coloured crystals, which contain 30·49 per cent. of silicon and 68·26 per cent. of carbon. These crystals differed considerably in appearance from those in the zone of silicon carbide; they were frequently parti-coloured, green, violet, and red being the prevailing tints.

The crystalline silicon carbide (*carborundum*) constituted the chief product of the reaction. The mass was easily broken up in a mortar, when the separate crystals were found to be bluish or yellowish-green; their size varied from a diameter of several millimetres to merely microscopic dimensions. The largest crystals occurred in fissures in the mass, where, apparently, there was room for them to form, and it remains an open question whether they had separated from a fused mass or were a product of sublimation.

To purify silicon carbide it may be heated to dull redness in oxygen, then boiled with potash solution, washed, digested with hydrochloric acid, again washed, and finally treated with hydrofluoric and sulphuric acids. After this treatment, its composition corresponds with the formula SiC.

Silicon carbide is insoluble in all acids, but is attacked by molten alkalis. It burns very slowly in oxygen when very finely divided, and if strongly heated in a platinum crucible it becomes a greenish-golden mass of great beauty, a portion of it being burnt during the ignition, It is attacked by hot ferric oxide. Its specific gravity at 15° is 3·22, but when finely divided it remains suspended in water for months.

The amorphous silicon carbide found in the third zone has all the properties of the crystalline specimens.

The fibrous material found in fissures and pockets in the fourth zone consists of silicon, aluminium, and carbon with a little lime and magnesia; it would thus appear to be a polycarbide of silicon and aluminium.

Much salt was volatilised during the reaction; the gas evolved consisted largely of carbon monoxide. A. G. B.

Crystallised Carbon Silicide. By H. MOISSAN (*Compt. rend.*, **117**, 425—428).—When carbon is dissolved in fused silicon in a wind furnace, crystals of carbon silicide several mm. in length can be obtained, and it follows that the two elements combine readily in a

fused medium at 1200—1400°. The silicide can, however, be prepared much more easily by heating in an electric furnace a mixture of 12 parts of carbon and 28 parts of silicon, the product being first heated with a mixture of nitric and hydrofluoric acids, and afterwards with a mixture of nitric acid and potassium chlorate. As a rule, the crystals are yellow, but by operating in a closed crucible with silicon as free as possible from iron, transparent, sapphire-blue crystals are obtained.

If iron silicide is heated with excess of silicon in the electric furnace, and the product is treated successively with aqua regia, nitric and hydrofluoric acids, and nitric acid and potassium chlorate, crystals of carbon silicide are obtained, and the result is similar with a mixture of iron, silicon, and carbon, or of iron, silica, and carbon.

The silicide is also produced by heating carbon and silica in the electric furnace, or by allowing the vapour of carbon to come into contact with vapour of silicon, when it is obtained in almost colourless, very hard and brittle, prismatic needles.

Carbon silicide prepared by any of these methods has the composition CSi, and is colourless when free from iron. It is very distinctly crystalline, and sometimes forms regular, hexagonal lamellæ, which occasionally, though very rarely, show triangular impressions and parallel striæ. They act strongly on polarised light. The crystals are very hard, and scratch chrome steel and rubies. Sp. gr. = 3·12.

Carbon silicide is not affected by oxygen at 1000°, nor when heated in air by a Schloesing's blowpipe. Sulphur vapour at 1000° is without action, and chlorine at 600° attacks the compound very slowly, although its action is complete at 1200°. Fused potassium nitrate or chlorate, boiling sulphuric, nitric, and hydrochloric acids, aqua regia, and mixtures of nitric and hydrofluoric acids do not attack it.

Fused lead chromate oxidises the silicide, but repeated treatment is necessary in order to obtain complete combustion of the carbon. Fused potassium hydroxide gradually converts it into potassium carbonate and silicate.   C. H. B.

Volatility of Ammonium Chloride. By K. KRAUT (*Zeit. anorg. Chem.*, **5**, 278—279).—When ammonium chloride is heated in a platinum basin in a water bath, an appreciable amount is lost by volatilisation; 50 per cent. of the whole if the heating is continued for 270 hours.   C. F. B.

Hemihydrate of Calcium Sulphate. By A. L. POTILITZIN (*J. Russ. Chem. Soc.*, **25**, 207—210).—The hydrate $2CaSO_4,H_2O$ may be formed by dehydrating gypsum at 98—99°, the water being lost very slowly ; or it may be formed by exposing anhydrous calcium sulphate to the air. The absorption of moisture is at first rapid, but the rate soon diminishes. The hemihydrate is capable of taking up small quantities of moisture from the atmosphere, and large quantities when allowed to remain over water. This excess of water is only partially lost when the hydrate is placed over sulphuric acid.   J. W.

Double Haloïds of Cæsium with Zinc and Magnesium. By H. L. WELLS and G. F. CAMPBELL (*Zeit. anorg. Chem.*, **5**, 273—277).— The following salts were prepared, and crystallise in colourless prisms or plates. $3CsCl,ZnCl_2$; $3CsBr,ZnBr_2$; $3CsI,ZnI_2$; $2CsCl,ZnCl_2$; $2CsBr,ZnBr_2$; $2CsI,ZnI_2$; $CsCl,MgCl_2 + 6H_2O$; $CsBr,MgBr_2 + 6H_2O$. Zinc probably also forms salts of the 1 : 1 type, but the solutions are so syrupy that pure crystals cannot be obtained.

No double chloride of cæsium and beryllium could be prepared.

C. F. B.

Double Haloïds of Cæsium and Cadmium. By H. L. WELLS and P. T. WALDEN (*Zeit. anorg. Chem.*, **5**, 266—272).—The following salts were prepared, and are all colourless. $3CsBr,CdBr_2$; $3CsI,CdI_2$; $2CsCl,CdCl_2$; $2CsBr,CdBr_2$; $2CsI,CdI_2$; $CsCl,CdCl_2$; $CsBr,CdBr_2$; $CsI,CdI_2 + H_2O$. Those of the 1 : 1 type, and $2CsI_2,CdI_2$, can be recrystallised from water; the others, when so treated, yield generally salts of the 1 : 1 type. C. F. B.

Occlusion of Gases by Metallic Oxides. By T. W. RICHARDS and E. F. ROGERS (*Amer. Chem. J.*, **15**, 567—578).—As in the case of cupric oxide, the oxides of zinc and nickel, and especially of magnesium, when prepared by ignition of the nitrates, are found to contain occluded gas; but the oxides of cadmium, mercury, lead, and bismuth retain no gas when prepared in this way. No gas is in any case retained when the oxide is prepared by ignition of the carbonate. The occluded gas was liberated by dissolving the oxide in hydrochloric acid, and was measured and analysed; it consisted mainly of oxygen and nitrogen, together with a very small quantity of a gas that dissolved in caustic potash, and was assumed to be carbonic anhydride [no reason is, however, given why this gas should not have been an oxide of nitrogen]. Oxides which still contained a trace of nitrate were found to be devoid of occluded gas; hence this gas must, in the other cases, have been derived from the decomposition of the last trace of nitric acid. The amount retained varied with the physical nature of the oxides, the more compact oxides retaining more gas, whilst those which form very fine powders retained no gas at all.

This occlusion of gases affects the atomic weights of a number of elements of which the oxides, as prepared by ignition of the nitrates, have been used in determining the atomic weights. C. F. B.

Compounds of Hydroxylamine with Metallic Carbonates. By H. GOLDSCHMIDT and K. L. SYNGROS (*Zeit. anorg. Chem.*, **5**, 129— 146).—*Dihydroxylamine zinc carbonate*, $Zn(NH_3O)_2CO_3$ is prepared by dissolving hydroxylamine hydrochloride and zinc chloride in water, adding an equivalent quantity of sodium carbonate, and passing air through the solution, when the new compound is precipitated. It is a white, microcrystalline powder, of sp. gr. 2·50 at 18°, insoluble in water. The function of the air in the above method of preparation is to remove carbonic anhydride from the solution. Cryoscopic experiments indicate that the zinc exists in the solution partly as the ion $Zn(NH_4O)_2$, and partly as dissociated zinc hydrogen carbonate;

the removal of a portion of the carbonic anhydride determines the molecular rearrangement.

When sodium carbonate solution is added to a solution containing ferrous chloride and hydroxylamine hydrochloride, a dark red coloration is produced, and the passage of hydrogen through the liquid determines the formation of a nearly black precipitate which contains ferrous oxide, hydroxylamine, and carbonic anhydride, but cannot be dried without decomposition. A cryoscopic examination of the solution indicates the presence of the ion $Fe(NH_3O)_2$.

When manganous chloride is mixed with hydroxylamine hydrochloride and sodium carbonate, a slight precipitate is first formed; this was filtered off, and a current of air was passed through the solution. A nearly white precipitate was thrown down, which dried to a grey powder, having the composition $4MnCO_3,3NH_3O,2H_2O$. A cryoscopic investigation showed that in this case no complex ion of metal and hydroxylamine exists in the solution.

The precipitate obtained by similar treatment of nickelous chloride varies in composition with the time during which air is passed through the liquid, and in no case is it of a very definite character.

Cadmium chloride gives a slight precipitate when mixed with hydroxylamine hydrochloride and sodium carbonate in solution, and when this has been filtered, the filtrate spontaneously deposits the dihydroxylamine cadmium chloride, $Cd(NH_3O)_2Cl_2$, previously prepared by L. de Bruyn and Crismer (Abstr., 1890, 558). This is somewhat soluble in cold water, and crystallises from hot water in white prisms; its sp. gr. is 2·72 at 18°.   A. G. B.

Preparation of Anhydrous Crystalline Metallic Silicates. By H. Traube (*Ber.*, **26**, 2735—2736).—When amorphous zinc silicate, prepared by precipitating a solution of zinc sulphate with sodium silicate, is heated with boric acid for 10 days at a high temperature, it is converted into a white, crystalline powder, which has the composition $ZnSiO_3$, and is insoluble in acids. The optical properties of the crystals show that they belong to the rhombic system, and the product is therefore a zinc-pyroxene isomorphous with the mineral enstatite.   E. C. R.

Lead Oxide as a Mordant. By A. Bonnet (*Compt. rend.*, **117**, 518—519).—When cotton is mordanted with an alkali plumbate and then washed with a large quantity of water, dissociation takes place, and the fibre becomes charged with lead peroxide, which partially oxidises and destroys it. A similar change takes place with plumbites, except that the fibre is not oxidised, lead monoxide being deposited. If the fibre thus treated is immersed in solutions of campeachy wood, it is dyed black; with shumac, it becomes green; with old fustic, a bright yellow. Tannin and catechu are also strongly attracted.

By immersing the tissue thus mordanted with lead oxide in hot neutral solutions of other salts, the tissue can be impregnated in a similar manner with oxides of gold, silver, mercury, vanadium,

manganese, chromium, iron, cobalt, nickel, and zinc, double decomposition taking place, and a lead salt going into solution.

C. H. B.

The True Atomic Weight of Copper. By G. HINRICHS (*Zeit. anorg. Chem.*, **5**, 293—298).—A protest against alleged errors in the atomic weight determinations of Stas and his followers, a recent determination by Richards of the atomic weight of copper (Abstr., 1893, ii, 12) being selected as a specimen of such faulty methods.

[In the opinion of the abstractor, the author does not substantiate all his objections, and the alternative "method of limits" which he proposes seems open to damaging criticism.] C. F. B.

Colour, &c., of Cupric Chloride Solutions. By N. N. TZUCHANOFF (*J. Russ. Chem. Soc.*, **25**, 151—152).—The author has investigated the connection between the colour and the electric conductivity of aqueous solutions of cupric chloride of different strengths at constant temperature. In weak solutions of a blue colour, the conductivity increases rapidly with the concentration, but the rate of increase falls off as the solution becomes green. A maximum conductivity is finally reached, the subsequent decrease with increasing concentration being accompanied by a change of tint to yellowish-brown. J. W.

Cæsium Cuprichlorides. By H. L. WELLS and L. C. DUPEE (*Zeit. anorg. Chem.*, **5**, 300—303).—Four salts were obtained. $2CsCl,CuCl_2$; yellow, rhombic prisms. $2CsCl,CuCl_2 + 2H_2O$; bluish-green crystals, turning yellow in the air. $3CsCl,2CuCl_2$; brown, triclinic crystals. $CsCl,CuCl_2$; hexagonal prisms, red by transmitted, black by reflected, light. C. F. B.

Cæsium Cuprochlorides. By H. L. WELLS (*Zeit. anorg. Chem.*, **5**, 306—308).—These were prepared by boiling a solution of cæsium and cupric chlorides in hydrochloric acid with copper wire, and then allowing the solution to crystallise. $CsCl,2CuCl$ and $3CsCl,2CuCl$; colourless crystals, turning yellowish when dried. $3CsCl,CuCl + H_2O$; prismatic crystals, very pale yellow in colour. C. F. B.

Cæsium Cupribromides. By H. L. WELLS and P. T. WALDEN (*Zeit. anorg. Chem.*, **5**, 304—305).—Two salts were obtained. $2CsBr,CuBr_2$; black, rhombic crystals with a greenish shade. $CsBr,CuBr_2$; black, hexagonal crystals with a shade of bronze; crystallisation from water converts these into the first-mentioned salt.

C. F. B.

Oxides contained in Cerite, Samarskite, Gadolinite, and Fergusonite. By W. GIBBS (*Amer. Chem. J.*, **15**, 546—566).—A description is given of various attempts that were made in order to separate the oxides contained in certain specimens of gadolinite, samarskite, and fergusonite. The methods employed were those of fractional precipitation or crystallisation, the salts used being the oxalates, oxychlorides, the double salts with sodium sulphate, and with the various cobaltamine sulphates, the lactates, and the double

salts with mercurous nitrate *plus* mercuric oxide, with acid molybdates, and with phosphotungstates and phosphomolybdates. The methods were often only imperfectly worked out, and the whole paper is somewhat disconnected, and cannot be satisfactorily abstracted.

As a means of determining the " mean atomic mass " of a fraction, it is recommended to precipitate with oxalic acid, carefully mix the dried oxalates in a mortar, and convert a weighed portion by ignition into oxides.   C. F. B.

Chemical Behaviour of Glass. By F. FOERSTER (*Ber.*, **26**, 2915—2922).—In continuation of his previous work on the action of water and of aqueous alkali and salt solutions on glass (Abstr., 1892, 1401), the author has now investigated the behaviour of acids towards glass. Round flasks of various kinds were employed, the glass, unless otherwise stated, being a calcium-alkali glass, such as is usually applied to chemical purposes ; the acid was allowed to act for six hours at 100°. With the same kind of glass, the action, which is always less than that of pure water, is independent both of the nature of the acid and also of its concentration between the limits N/1000 and 10N. With concentrated acids at 160—190°, the nature of the acid is without effect, whilst the amount of change decreases with increasing concentration. The same result was obtained with hydrochloric acid at 260—270°. Emmerling's results, which led him to the contrary conclusion, are probably incorrect. Acids appear, therefore, to be indifferent towards glass ; the action which actually takes place is due simply to the water which is always present, and which dissolves alkali ; this rapidly attacks the glass, but the stronger the acid the more quickly will the alkali be neutralised. This view receives additional support from the fact that, in comparison with water, acids dissolve larger quantities of alkali and less silica from the glass.

The difference in behaviour towards concentrated acids between glass and other calcium-alkali silicates is noteworthy ; the compound Na_2O,SiO_2 is more readily decomposed by concentrated than by dilute acids, whilst sodium silicate with the composition $Na_2O,3SiO$ behaves like glass in this respect. The reaction is conditioned both by the nature of the bases, and by the relative proportion of silica present ; this is shown from the fact that, towards acids, lead crystal glass behaves like calcium-alkali glass, but their action on flint glass, which is poorer in silica, increases with the concentration and differs according to the nature of the acid. Jena thermometer glass 16[III], which contains zinc, calcium and sodium, is more rapidly acted on by concentrated than by dilute hydrochloric acid at 190°, whilst a calcium-sodium glass of equivalent composition behaves in the usual manner. Pure sulphuric acid attacks calcium-alkali glass less rapidly than pure water at 100° ; the action slowly increases with rising temperature ; the vapour acts comparatively vigorously, and the glass becomes covered with a network of alkali sulphate crystals.

Carbonic anhydride resembles acids in its action; the " weathering " of glass is chiefly caused by the action of moisture. Glass of every kind combines chemically with more or less water, a graduated series

of compounds being obtained, which form connecting links between fresh glass and the substances that are found in solution. The paper concludes with tables showing (1) the composition of the six better kinds of glass employed for chemical purposes; (2) their relative stability towards water, alkalis, and alkaline carbonates. The best glass mentioned has the following composition:—$K_2O = 6.2$; $Na_2O = 6.4$; $CaO = 10.0$; $MnO = 0.2$; $Al_2O_3 + Fe_2O_3 = 0.4$; $SiO_2 = 76.8$ per cent.; the ratio $R_2O : RO : SiO_2 = 0.95 : 1 : 7.16$; it contains 10·4 mols. of alkali in 100 mols., and is, therefore, almost identical with the glass used by Stas in his atomic weight determinations.

J. B. T.

Manganese. By O. PRELINGER (*Monatsh.*, **14**, 353—370).— Manganese amalgam is prepared by passing an electric current (11 volts; 22—23 c.c. electrolytic gas per minute) from a cathode of pure mercury (20 c.c.) through a saturated aqueous solution of pure manganous chloride (75 c.c.) to an anode of carbon or platinum-iridium contained in a porous vessel. The temperature rises to 70°, and after 5—6 hours the mercury assumes a pasty consistence. The paste is quickly washed in running water without undergoing appreciable decomposition, the excess of mercury squeezed out through linen, and the residue dried over calcium chloride in an atmosphere of hydrogen.

The solid amalgam thus obtained is broken into small pieces and subjected to great pressure (2000 kilos. per sq. cm.) for several hours. The peripheral portion of the pressed cake is broken off, and the central portion broken up and again compressed. The operation is repeated until samples punched from the centres of successive discs yield constant analytical results. Analyses of three distinct preparations yielded practically identical results, pointing to the composition Mn_2Hg_5. It corresponds with the cadmium compound Cd_2Hg_5.

Manganese-mercury, Mn_2Hg_5, has a slate-grey colour, and assumes a metallic lustre when rubbed or cut. At ordinary temperatures, it oxidises very slowly in the air, metallic mercury being eliminated. At 100—110°, it decomposes slowly into its elements. It decomposes water and acids at the ordinary temperatures. The sp. gr. is 12·828, a number greater than that, 12·532, calculated from the sp. gr. of its constituents, so that contraction takes place in the formation of the compound. Manganese-mercury is electro-positive to manganese, so that heat is probably absorbed in its formation. A solution of the compound in mercury is not attacked by dry air, but is quickly oxidised by moist air to manganic oxide, Mn_2O_3, which forms a fine dust on the surface of the liquid.

When manganese-mercury is gently ignited in a stream of pure dry hydrogen (free from oxygen), pure manganese remains behind, uncontaminated with mercury or hydrogen. The *manganese* forms a grey, porous mass, which may be ground into a slate-coloured powder, perfectly stable in air. If the temperature does not reach dull redness in the ignition, however, the metal is set free in a pulverulent spontaneously-inflammable form. The metal cannot be made to exhibit lustre. The sp. gr. of the powdered metal is 7·4212 and the atomic volume (at. wt. = 54·8) 7·385. Manganese powder is

neither magnetic nor magnetisable at ordinary temperatures. It attacks water, slowly in the cold, rapidly when heated. It has little action on concentrated sulphuric acid in the cold, but attacks it rapidly on heating gently, sulphurous anhydride being formed. It liberates hydrogen from dilute sulphuric acid. The action on concentrated nitric acid is explosively violent. It displaces hydrogen from hydrochloric and acetic acids and sodium hydroxide. From aqueous ammonium chloride it liberates ammonia and hydrogen. It reduces metals with great rapidity from warm solutions of their salts (preferably sulphates); the excess of manganese may be dissolved by ammonium chloride. Arsenic, antimony, copper, lead, bismuth, tin, iron, nickel, cobalt, chromium, cadmium, and zinc are thus reduced. The reduction of the magnetic metals may be conveniently demonstrated by means of a compass needle, the latter being deflected after, although not before, the addition of the manganese.   Jn. W.

Iron Nitride. By G. J. Fowler (*Chem. News*, **68**, 152—153).— By exposing iron, reduced from the hydroxide by hydrogen, to a fairly rapid current of ammonia, at a temperature slightly above the melting point of lead, until its weight becomes constant, iron nitride, Fe_2N, is obtained as a feebly magnetic, grey powder. It dissolves in hydrochloric acid, yielding ferrous chloride, ammonium chloride, and hydrogen; it burns in chlorine to ferric chloride and nitrogen; ammonia or ammonium salts are produced when it is heated in hydrogen at the temperature of its formation; in steam at 100°, or in hydrogen sulphide at 200°, or by treatment with hydrogen peroxide and sulphuric acid. By simply heating, it is resolved into iron and nitrogen, but remains unchanged in nitrogen at 440°, or when heated in carbonic oxide or with phenol at 200°; with ethylic iodide, however, in a sealed tube at 200°, ferrous iodide, ammonium iodide, ethylene, and hydrogen are formed. Its heat of formation is about 3 cal. These results agree with many of Stahlschmidt's observations (*Ann. Phys. Chem.*, **125**, 37).   D. A. L.

Constitution of Cobalt, Chromium, and Rhodium Bases. By S. M. Jörgensen (*Zeit. anorg. Chem.*, **5**, 147—196; compare Abstr., 1892, 782, 783).—The first part of this paper deals with the views put forward by A. Werner concerning the structure of ammonio-metallic salts (Abstr., 1893, ii, 379); the author does not regard them as being at variance with the views promulgated by himself and Blomstrand.

The author next describes the best method of preparing the croceocobalt salts from xanthocobalt chloride, and a series of salts, which he terms flavocobalt salts, isomeric with the croceocobalt salts.

Flavocobalt nitrate, $(NO_2)_2Co(NH_3)_4NO_3$, is prepared by dissolving carbonatotetraminecobalt nitrate (*Zeit. anorg. Chem.*, **2**, 282) in cold dilute nitric acid, and adding crystallised sodium nitrite. After being warmed for a few minutes on the water bath, the liquid is cooled, and dilute nitric acid is added. A mixture of the acid and normal salts crystallises, and may be converted entirely into

the normal salt by washing with 95 per cent. alcohol. The flavo-cobalt nitrate dissolves in 33 parts of cold water, whilst the croceo-cobalt nitrate requires 400 parts of cold water for its solution.

A detailed comparison of the reactions of croceo- and flavo-cobalt nitrates follows, and the *dinitrate*, $(NO_2)_2Co(NH_3)_4NO_3,HNO_3$; the *sulphate*, $[(NO_2)_2Co(NH_3)_4]_2SO_4$; the *chromate*,

$$[NO_2)_2Co(NH_3)_4]_2CrO_4;$$

the *dichromate*, $[(NO_2)_2Co(NH_3)_4]_2Cr_2O_7$; the *platinosochloride*, $[(NO_2)_2Co(NH_3)_4]_2PtCl_4$; the *platinochloride*,

$$[(NO_2)_2Co(NH_3)_4]_2PtCl_6;$$

and the *aurochloride*, $(NO_2)_2Co(NH_3)_4AuCl_4$, are described. To pre-pare the xanthocobalt salts, chloropurpureocobalt chloride is warmed with water and ammonia; the liquid is filtered from some precipitated cobalt oxide, cooled, and neutralised with dilute hydrochloric acid; sodium nitrite and hydrochloric acid are next added, whereon a red precipitate is thrown down. This is an isomeride of xanthocobalt chloride, and is provisionally named *nitritocobalt chloride;* it is readily converted into the xantho-salt by dissolving it in water con-taining a few drops of ammonia, and adding strong hydrochloric acid, which throws down the xanthochloride.

The reactions of the xantho-salts are detailed, and the *sulphates*, $4[(NO_2)Co(NH_3)_5,SO_4],3H_2SO_4$ and $NO_2 \cdot Co(NH_3)_5SO_4$, are described.

Xanthocobalt chloride dissolves in 50 parts of cold water; nitrito-cobalt chloride dissolves in 200 parts. Differences between the reac-tions of the two salts are described, and it is shown that the nitrito-salt is not a roseo-salt.

The author has prepared a *luteorhodium rhodium chloride*, $Rh(NH_3)_6Cl_3,RhCl_3$, and a *chloropurpureorhodium rhodium chloride*, $3RhCl(NH_3)_5Cl_2,2RhCl_3$.

The following salts are described:—*Luteocobalt cobaltinitrite*, $Co(NH_3)_6Co(NO_2)_6$; *xanthocobalt cobaltinitrite*,

$$[NO_2 \cdot Co(NH_3)_5]_3,[Co(NO_2)_6]_2;$$
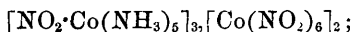
croceocobalt cobaltinitrite, $[(NO_2)_2Co(NH_3)_4]_3Co(NO_2)_6$; *flavocobalt cobaltinitrite*, $[(NO_2)_2Co(NH_3)_4]_3Co(NO_2)_6$; *luteocobalt diaminecobalti-nitrite*, $Co(NH_3)_6[(NO_2)_2(NH_3)_2Co(NO_2)_2]_3$; *xanthocobalt diamine-cobalt nitrite*, $NO_2Co(NH_3)_5[(NO_2)_2(NH_3)_2Co(NO_2)_2]_2$; *croceocobalt diaminecobalt nitrite*, $(NO_2)_2Co(NH_3)_4(NO_2)_2(NH_3)_2Co(NO_2)_2$; *flavo-cobalt diaminecobalt nitrite*, $(NO_2)_2Co(NH_3)_4(NO_2)_2(NH_3)_2Co(NO_2)_2$; *triaminecobalt nitrate*, $Co(NH_3)_3(NO_3)_3,3H_2O$; *dichrocobalt chloride*, $Co(NH_3)_3(OH)_2Cl_3$; *nitrotriaminecobalt nitrite*, $NO_2 \cdot Co(NH_3)_3(NO_2)_2$; and *chloronitrotetraminecobalt chloride*, $(NO_2)ClCo(NH_3)_4Cl$.

A. G. B.

Atomic Weight of Molybdenum. By E. F. SMITH and P. MAAS (*Zeit. anorg. Chem.*, **5**, 280—282).—Pure sodium molybdate was heated in a current of hydrochloric acid: the reaction $Na_2MoO_4 + 4HCl = 2NaCl + MoO_3,2HCl + H_2O$ took place, and the residue, which consisted of pure sodium chloride, was weighed. The atomic

weight was found to be 96·087 (O = 16) as a mean of 10 determinations, which varied from 96·130 to 96·031. C. F. B.

Tin and Stannic Oxide. By F. EMICH (*Monatsh.*, **14**, 345—352).—When pure block tin is heated in a stream of air or in an open porcelain crucible, drops of molten metal ooze after some hours from beneath the superficial crust of stannic oxide, and, becoming superficially oxidised, gradually assume curious forms resembling bulbs and worms. After 12 hours' heating, the oxide is crystalline, and consists of microscopic, needle-like, rhombic plates of sp. gr. 7·01. The crystals seem to be formed directly from the metal, as the amorphous oxide prepared from "metastannic acid" may be heated in contact with tin in an indifferent atmosphere without undergoing change of form. They are not due to the oxidation of metallic vapour, since the metal is not volatile at the temperatures employed.

When tin containing traces of iron (0·05 per cent.) is heated in the manner described above, most of the iron is eliminated with the first portions of stannic oxide, a mere trace (0·001 per cent.) being left in the tin. The stannic oxide assumes a colour varying from brown to yellow with the amount of iron, thus serving as a good qualitative test for that impurity. The oxide formed after the iron has been eliminated is snow-white. JN. W.

Thorium Compounds. By P. JANNASCH, J. LOCKE, and J. LESINSKY (*Zeit. anorg. Chem.*, **5.** 283—287).—This is a preliminary paper. It contains a detailed account of the means adopted to obtain pure thorium oxalate from thorite and orangite. From the hydroxide the bromide (? $ThBr_4 + 10H_2O$) and iodide were prepared; they form very deliquescent crystals. C. F. B.

Double Haloïds of Antimony and Rubidium. By H. L. WHEELER (*Zeit. anorg. Chem.*, **5**, 253—263; and *Amer. J. Sci.*, [3], **46**, 269—279).—The double haloïds enumerated below have been prepared by concentrating solutions in 10 per cent. halogen acids of the two haloïds in varying proportions; the proportion by molecules of rubidium to antimony haloïd in the solution is given by the numbers in square brackets. The 23 : 10 salts might equally well have a 16 : 7, 9 : 4, or 7 : 3 formula; the 3 : 2 salts are isomeric with the corresponding arsenic compounds.

$RbCl,2SbCl_3 + H_2O$ [1 : 10, 6, or 8]; colourless, monoclinic plates melting at 77°, $a : b : c = 1·699 : 1 : 0·820$; $\beta = 89° 28\frac{1}{2}'$.

$RbCl,SbCl_3$ [1 : 4 or 3]; colourless, monoclinic crystals, $a : b : c = 1·732 : 1 : 1·085$; $\beta = 65° 34'$.

$3RbCl,2SbCl_3$ [1 : 1⅕]; yellow rhombohedra, exhibiting rhombohedral tetartohedry. $23RbCl,10SbCl_3$ [1, 4, or 6 : 1]; colourless, hexagonal plates.

$3RbBr,2SbBr_3$ [2·3 or 5 : 1]; lustrous, yellow, hexagonal plates. $23RbBr,10SbBr_3$ [6, 8, or 13 : 1]; lustrous, yellow needles.

$3RbI : 2SbI_3$, red rhombohedra. C. F. B.

Recovery of Osmium from Residues. By W. GULEWITSCH (*Zeit. anorg. Chem.*, **5**, 126—128).—The osmium residues obtained in histological laboratories are the solution of osmium tetroxide drained or filtered from the treated objects, and the *débris* of the objects themselves. The solutions are treated with zinc and hydrochloric acid, the osmium is collected, washed successively with hydrochloric acid, water, alcohol, and ether, and then allowed to dry at a low temperature The osmium is then transferred to the hind portion of a combustion tube which has a constriction containing an asbestos plug in front of the osmium ; the forward portion of the tube is bent into a ∪, and the end is drawn out to a fine tube which is bent over and placed in a flask; the ∪-tube and the flask are surrounded by a freezing mixture. A current of dry oxygen is passed through the apparatus, the osmium is gently heated, and the resulting tetroxide condensed in the ∪ bend ; if the process be properly conducted, none of the tetroxide will be carried over into the flask.

The osmium cannot be directly sublimed as tetroxide from the objects because of the organic matter which they contain. These residues are warmed in a retort with 10 times their weight of aqua regia, and the resulting solution is distilled until two-thirds have passed over, the receiver being well cooled. The distillate is again distilled until two-thirds have passed over, the second distillate is reduced by zinc, and the precipitated osmium is treated as described above. A large excess of zinc must be used, and the liquid must be warmed, in order that the osmium may be precipitated in a condition in which it will be retained by a filter. A. G. B.

Mineralogical Chemistry.

Vanadiniferous Coal. By A. MOURLOT (*Compt. rend.*, **117**, 546—548).—This coal is analogous to that recently described by Kyle from the province of Mendozza, in the Argentine Republic. Its sp. gr. is only 1·15—1·20. It contains ash, 0·63; H, 4·73; N, 1·67; C, 85·03. The composition of the ash is—*Part soluble in acids:* V_2O_5, 38·5; SO_3, 12·1; P_2O_5, 0·8; Fe_2O_3, 4·1; Al_2O_3, 4·0; CaO, 8·44; K_2O, 1·8. *Part insoluble in acids:* SiO_2, 13·6; Al_2O_3, 5·5; Fe_2O_3, 9·4; MgO, 0·9. The percentage of vanadic anhydride in the original coal is 0·24.

C. H. B.

Nesquehonite. By C. FRIEDEL (*Zeit. Kryst. Min.*, **22**, 279; from *Bull. soc. fran. min.*, **14**, 60).—In the anthracite mines at Mure, in Isère, there occurs a fibrous mineral resembling aragonite, which, on exposure to air, becomes of a silky lustre, and has the composition $MgCO_3 + 3H_2O$. Analysis yielded

MgO.	H_2O.	CO_2.
28·97	38·85	31·85

The mineral has a prismatic cleavage of about 115° parallel to the fibres. It is identical with the nesquehonite of Genth and Penfield.

B. H. B.

Xenotime from North Carolina. By W. E. HIDDEN (*Amer. J. Sci.*, [3], **46**, 254—257).—A few small crystals of transparent xenotime have been found with monazite at a locality about 1 mile south-east of Sulphur Springs, Alexander Co., North Carolina. The measurements of these new crystals do not vary essentially from those of vom Rath and Klein.

Green xenotime occurs as a rare constituent of the auriferous gravels of the Brindletown gold region of Burke Co., North Carolina. It has not as yet been found *in situ*. Within brown, opaque crystals, the new green variety was found. It appears to represent the original condition, whilst the brown variety is an alteration product. The new material is of a bottle-green colour and transparent, and when finely pulverised is soluble in hot hydrochloric acid. The author gives the results of analyses of both the green and the brown variety. A very complex mixture is shown. It seems probable that xenotime is either a silico-phosphate, like some monazite and anerlite, or it is often mechanically mixed with some cyrtolite and other silicates of the rare earths.

B. H. B.

Nephrite from British Columbia. By B. J. HARRINGTON (*Zeit. Kryst. Min.*, **22**, 310—311; from *Trans. R. Soc. Canada*, 1890, 61). —The author communicates the following analyses of nephrite.

	SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	Loss.	Total.
I.	55·32	2·42	5·35	0·52	14·00	20·16	2·16	99·93
II.	56·98	0·18	4·59	0·17	12·99	22·38	2·64	99·93
III.	56·54	0·40	3·61	0·16	13·64	22·77	2·92	100·04
IV.	56·96	0·51	3·81	0·53	13·29	22·41	2·91	100·42

I. Rounded mass from an Indian tomb at Lytton, on the Fraser River. Colour, olive-green. Hardness over 6, and very tough. Sp. gr., 3·0278. II. Fragment of an axe from the same locality. Colour, greyish-green. Sp. gr., 3·003. III. A worked fragment of pale green colour from the vicinity of Lytton. It shows small laminæ of tremolite. Sp. gr., 3·01. IV. Small fragment from the Lewes River, near the frontier of Alaska. Colour, greyish-green. Sp. gr., 3·007. The author shows that the composition of these nephrites is the same as that of specimens from other parts of the world. Jadeite has not yet been found in British Columbia.

B. H. B.

Talc from Madagascar. By E. JANNETTAZ (*Zeit. Kryst. Min.*, **22**, 279; from *Bull. soc. fran. min.*, **14**, 67).—A fibrous, pale green mass with pearly lustre from Ambohimanga-Atsimo, in Madagascar, proved to be talc. It is probably a pseudomorph. Analysis yielded

H_2O.	SiO_2.	FeO.	MgO.
5·1	62·3	2·6	29·4

There have also been found in Madagascar prismatic crystals of

sapphire and zircon, pink tourmaline, and rubellite in nine-sided prisms with rhombohedral termination. B. H. B.

Topaz in the Fichtelgebirge. By K. OEBBEKE (*Zeit. Kryst. Min.*, **22**, 273—275).—Small, yellowish crystals of topaz were discovered in 1879 by v. Gümbel in the granite of Rudolphstein. The author describes two new occurrences of topaz at the Epprechtstein and the Gregnitzgrund, in the Fichtelgebirge, which support v. Gümbel's view that topaz would probably be found in other granites in that district. B. H. B.

Canadian Spessartine. By B. J. HARRINGTON (*Zeit. Kryst. Min.*, **22**, 309; 'from *Canadian Rec. Sci.*).—Garnet occurs in felspar and mica at the Villencuve Mica Mine at Villeneuve, Quebec. The mine has been opened on a vein of coarse-grained granite consisting of quartz, muscovite, orthoclase, albite, and small quantities of tourmaline and garnet. Uraninite and monazite are also met with. The garnet examined was derived from the mica. The largest crystal had a diameter of about 10 mm., and was bright red. Its sp. gr. is 4·117, and analysis shows it to be a manganese garnet similar in composition to the original spessartine. B. H. B.

Vesuvian in Ireland. By J. P. O'REILLY (*Zeit. Kryst. Min.*, **22**, 300; from *Proc. R. Irish Acad.*, 1891, 446).—Vesuvian was found as a honey-yellow, lamellar substance in a manganiferous iron ore from the Cambrian strata in Calliagh, Monaghan Co. Analysis gave the following results.

SiO_2.	Al_2O_3.	CaO.	Fe_2O_3.	MnO.	CuO.	Na_2O.	Loss.
40·06	16·03	37·46	4·23	1·16	0·21	1·00	2·07

B. H. B.

Chemical Nature of Axinite. By H. RHEINECK (*Zeit. Kryst. Min.*, **22**, 275—277).—Rammelsberg's investigations led to the formula $Al_2Si_4BM_3HO_{16}$ for axinite. This, however, is shown by the author to be not in accord with the results of analyses recently published by Whitefield, Genth, and Baumert. Calculations are given showing the composition of axinite from Oisans, Cornwall, Franklin in New Jersey, Guadalcazar in Mexico, and Radauthal in the Hartz.
B. H. B.

Minerals from the Manganese Mines of St. Marcel, Italy. By S. L. PENFIELD (*Amer. J. Sci.*, [3], **46**, 288—295).—*Alurgite.*—In 1865, Breithaupt described, under this name, a deep red mica from St. Marcel, in Piedmont, Italy. Since then it has never been investigated. Further examination, however, shows that it is a distinct species. The crystallisation is monoclinic, and the structure micaceous. The colour is a characteristic, deep, brownish copper-red. The hardness is 3, and the sp. gr. 2·84. Analysis yielded

SiO_2.	Al_2O_3.	Fe_2O_3.	Mn_2O_3.	MnO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
53·22	21·19	1·22	0·87	0·18	6·02	11·20	0·34	5·75	99·99

Chemically, this mica is distinct from any known species. It is more closely related to lepidolite than to any of the others.

Jadeite.—The alurgite is embedded in a pyroxene rich in soda, resembling in structure a rather coarsely crystallised jadeite, and agreeing in composition with a jadeite from Mexico, analysed by Damour (Abstr., 1883, 1066).

Violan.—This name was given, in 1833, by Breithaupt to a rare blue mineral found at Piedmont. Published analyses of this mineral show considerable variation. The results of the author's analysis show that the mineral is essentially a blue variety of diopside, containing small quantities of various well-recognised pyroxene molecules. The composition may be expressed as a mixture of the following metasilicates.

$MgCa(SiO_3)_2$, diopside . . . .   90·8 per cent.
$NaAl(SiO_3)_2$, jadeite . . . .   4·1   ,,
$NaFe(SiO_3)_2$, acmite . . . .   2·4   ,,
$NaMn(SiO_3)_2$?   . . . .   2·7   ,,

B. H. B.

Monticellite Crystals obtained in Lead Smelting. By W. v. GÜMBEL (*Zeit. Kryst. Min.*, **22**, 269—270).—At Freihung, in the Upper Palatinate, lead ores occur in sandstone in such quantity that at one time the mining industry was of considerable importance. Owing to lack of pumping machinery, the mines were, however, abandoned in the middle of the present century. On reopening the mines recently, interesting specimens of galena and cerussite have been met with. The ore is smelted in a Pilz furnace. The silicate slags formed, on slow cooling, crystallise out as well-developed acicular crystals, giving, on analysis, the following results.

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	P_2O_5.
33·04	1·10	7·91	31·53	1·16	23·52	1·18	0·58	0·24	0·31

The sp. gr. was found to be 3·58, and the crystals were isomorphous with those of the members of the olivine group, the forms observed being $2\check{P}\infty$, ∞P, $\infty\check{P}\infty$. This crystallised slag is thus a monticellite, in which the magnesia is replaced by ferrous oxide.

B. H. B.

Serpentine from Bray Head. By J. P. O'REILLY (*Zeit. Kryst. Min.*, **22**, 300; from *Proc. R. Irish Acad.*, 1891, 503).—An intrusive rock of Cambrian age, at Bray Head, Dublin, was formerly described as greenstone. The author shows that it is really a serpentine, probably formed by the alteration of a diabase porphyry.   B. H. B.

New Meteorite from Hamblen Co., Tennessee. By L. G. EAKINS (*Amer. J. Sci.*, [3], **46**, 283—285).—This meteorite was found in September, 1887, on a ridge 6 miles from Morristown, Tennessee. The various pieces found weigh about 36 lbs.; most of them exhibit much surface oxidation, a fresh fracture showing a grey colour, with numerous metallic particles of nickel-iron. The latter gave the following results on analysis.

Fe.	Ni.	Co.	Cu.	P.	S.	Total.
90·92	7·71	0·80	trace	0·19	0·04	99·66

The siliceous portion of the meteorite gave the following results.

	SiO₂.	Al₂O₃.	Cr₂O₃.	FeO.	NiO.	MnO.	CaO.	MgO.
I.	16·79	8·33	—	4·88	0·39	—	5·19	1·34
II.	31·47	9·25	0·82	6·55	—	0·47	2·24	11·16

	K₂O.	Na₂O.	P₂O₅.	S.	Total.
I.	—	—	0·46	0·25	37·63
II.	0·02	0·12	—	—	62·10

I, portion soluble in hydrochloric acid; II. insoluble portion. In many stony meteorites, olivine forms the bulk of the soluble portion. In this case, analysis shows olivine to be present in but small proportion, if at all.   B. H. B.

Physiological Chemistry.

Respiratory Exchange in Shivering. By C. RICHET (*Compt. rend. Soc. Biol.*, 1893, 33—35).—Shivering is regarded as an act to produce more heat when the blood has been cooled. The experiments were tried on chloralised dogs, in which there is great lowering of the amount of carbonic anhydride produced. On shivering, this rises, especially if the shivering is violent, and the respiratory quotient rises also. W. D. H.

Proteïd-poor Nutrition. By T. ROSENHEIM (*Pflüger's Archiv*, **54**, 61—71).—A number of experiments on dogs are recorded in which a diet poor in nitrogen was given. The analyses of the food and excreta, and the daily weight of the animal, are given in tables. These experiments confirm the previous observations of the author, that such diets are very harmful ; the animal becomes ill and apathetic, similar to the condition observed in starvation. *Post-mortem* examination showed extensive fatty degeneration, especially of the liver and alimentary tract. W. D. H.

Influence of Muscular Work on the Excretion of Sulphur. By C. BECK and H. BENEDICT (*Pflüger's Archiv*, **54**, 27—61).—During muscular work the excretion of sulphur is increased. This is followed (when the work has ceased) by a corresponding diminution. The increase falls especially on the oxidised sulphur; the non-oxidised sulphur due to proteïd metabolism may be lessened. The relationship of these two forms of sulphur is recommended as an indication of the disintegration of proteïd in the body. W. D. H.

Circulating Proteïd. By E. PFLÜGER (*Pflüger's Archiv*, **54**, 333—419).—This is a long, critical, and polemical article directed against Voit's theory of the distinction between organ proteïd and circulating proteïd. The tendency of the article is to show that

metabolic processes in proteïd matter occur in the cells, that is, in organised proteïd; but it is admitted that in the organised cell substance there are different kinds of organised proteïd molecules, different degrees of organisation.   W. D. H.

How does Proteïd Nutrition influence Proteïd Metabolism in Animal Cells? By B. SCHÖNDORFF (*Pflüger's Archiv*, **54**, 420—483).—The increase of urea in the blood after proteïd food is not due to a diffusion of urea from the tissues into the blood, but to a real new formation of urea in the liver from the nitrogenous decomposition products of cellular activity.

By leading the blood of a starving animal through the organs and liver of a well-nourished one, the amount of urea in the blood is increased. By leading the blood of a starving animal through the organs and liver of a starving animal, there is no change in the amount of urea. By leading the blood of a well-nourished animal through the organs and liver of a starving animal, the amount of urea in the blood is diminished.

Therefore, the amount of proteïd decomposition depends on the nutritive condition of the cells, and not on the proteïd contents of the " intermediate lymph stream." The amount of urea in the blood depends on the condition of the animal, falling during hunger (minimum 0·0348 per cent.), and rising to a maximum during the time of greatest urea formation (0·153 per cent.). The decomposition products from which the liver forms urea are probably ammonium salts.   W. D. H.

Sulphur in Human and Animal Tissues. By H. SCHULZ (*Pflüger's Archiv*, **54**, 555—573).—In the dried organs of a man, aged 39, the percentage of sulphur was found to vary from 0·57 in the brain to 1·03 in the jejunum. In the muscles of various animals, the percentage varied from 0·86 to 1·33; in the human aorta, from 0·45 to 0·67; and in the human vena cava, from 0·28 to 0·73.
                                                      W. D. H.

Non-coagulable Blood. By C. J. MARTIN (*J. Physiol.*, **15**, 375—379).—When nucleo-albumins (Wooldridge's tissue fibrinogens) are introduced into the circulation, a state of non-coagulability is sometimes produced. This is considered by Wright and Pekelharing to be due to the cleavage of the nucleo-albumin into nucleïn and a peptone-like substance, to the latter of which the non-coagulability of the blood is due. This view has been already questioned by Halliburton and Brodie (*Brit. Med. J.*, ii, 1893, 631), and the present paper shows conclusively that no peptone or proteose is present in the blood in the condition in question.

The method adopted is to mix the blood with an equal volume of 10 per cent. trichloracetic acid. This is raised to the boiling point, and filtered hot. The filtrate gave no indications of the presence of either proteose or peptone. This method, a modification of Starling's, is well calculated to detect these substances, as control specimens of blood to which peptone or proteose was added showed. The

object of boiling and keeping the mixture hot during filtration is that the proteoses are partly precipitable by the acid in the cold, but this precipitate dissolves on heating.   W. D. H.

Results of feeding Cows at Grass on Meal. By J. P. ROBERTS and H. H. WING (*Bied. Centr.*, **22**, 728—732).—Eight cows were pastured only, whilst another eight received mixed meals in addition to the pasturage. It was found that whilst the eight cows receiving meals gave a larger daily yield of milk, yet the percentage of fat in the milk was lower than that found in the milk from cows fed on grass only ; at the same time, the excess of milk thus obtained paid for the extra food given.   E. W. P.

Mule's Milk. By A. B. AUBERT and D. W. COLBY (*Chem. News*, **68**, 168—169).—Two samples of a mule's milk were examined, one collected about six weeks, the other about nine weeks, after the flow of milk had commenced ; the mule was 11 years old, in work, fed on oats and hay. and yielded about 2 quarts of milk daily, being milked at frequent intervals. The milk was pure white, alkaline ; turning sour, after long standing, with the separation of a fine, floating, flocculent coagulum instead of a curd ; the fat globules were very small ; the casein is not readily precipitated by dilute acetic acid or by carbonic anhydride ; this was especially the case with the first sample. The analytical numbers given are

Sp. gr. at 15°	1·032	1·033
Total solids..........	10·65	10·86
Proteïds.	2·94	2·31
Fat.................	1·86	1·98
Sugar.	—	6·03
Ash	—	0·53

D. A. L.

Secretion of Urine. By L. LIEBERMANN (*Pflüger's Archiv*, **54**, 585—606).—In a previous paper (Abstr., 1893, ii, 27), an acid constituent of the kidney substance, named lecithalbumin, is described. The properties of lecithalbumin generally are discussed in *Pflüger's Archiv*, **54**, 573—585. This material is obtained from the tissue as a residue after artificial gastric digestion. It is like nucleïn ; it is believed to come from the nucleus, and it possesses the power of interacting with a basic phosphate, Na_2HPO_4, yielding an acid filtrate. Similar substances are obtained from blood serum or from defibrinated blood. The reaction of the fresh kidney is not constant ; it is usually neutral ; it may be alkaline or slightly acid ; *post mortem*, it invariably soon becomes acid. This inconstancy indicates that the reaction of the kidney is a variable factor during life, and is probably related to the stages of its secretion. The acidity of the kidney is believed to be due to the lecithalbumin, which is stated to be the most abundant constituent of the cell substance. This is confirmed by microchemical staining ; the nucleus, and to a less extent the cell protoplasm, taking up basic dyes.

It is further advanced that the acidity of the urine is due to the

interaction of sodium urate and disodium hydrogen phosphate; these are contained in the blood plasma, and their interaction is brought about by the acid constituent of the cells (lecithalbumin) which the secretion on its way from blood to urinary tubules must necessarily come in contact with.
W. D. H.

Fermentation and Carbohydrates in Urine. By E. SALKOWSKI (*Pfluger's Archiv*, **54**, 607—614).—Polemical. An answer to E. Baumann.

Variations of Glycogenia in Anthrax. By H. ROGER (*Compt. rend.*, **117**, 488—490).—When the anthrax bacillus is cultivated in milky decoctions of liver, all the glycogen is somewhat rapidly destroyed, and the liquid likewise contains no sugar. Now, glycogen is never found in the liver of animals that die of anthrax, but sugar can easily be detected in the liver and the blood.

In the early stages of anthrax, before the bacilli have appeared in the blood, the liver contains large quantities of glycogen, but in later stages, when the blood has become charged with bacilli, all the glycogen has disappeared from the liver. It would seem that as soon as the temperature reaches 39·5° the glycogen disappears, but if the temperature falls to 38°, glycogen appears again in the liver.

In most cases, however, the disappearance of the glycogen coincides with the reduction of the central temperature and the appearance of numerous bacilli in the blood. The disappearance of the glycogen is always accompanied by marked hyperglycæmia. It follows that in anthrax the glycogen is rapidly converted into glucose, and the tissues then become incapable of consuming the sugar furnished by the liver.

The bacilli destroy sugar in liquid cultivations, but seem to be without the power of attacking it in the animal organism.
C. H. B.

Toxicity and Therapeutic Use of Sodium Fluoride. By BLAIZOT (*Compt. rend. Soc. Biol.*, 1893, 316—319).—Sodium fluoride has antiseptic properties, a statement of Arthus and Huber which is confirmed in the present paper by further experiments. It is recommended as a lotion in various affections of the skin and mucous membranes; its toxicity is small, 8 centigrams per kilo. of body weight having in rabbits to be injected intravenously to produce poisonous symptoms; the symptoms are slight fever, salivation, and dyspnœa. The animal recovers in a few hours. After a dose of 1 decigram, however, the symptoms are more intense, and the animal dies in a comatose condition.
W. D. H.

Physiological Action of Apocodeïne. By L. GUINARD (*Compt. rend. Soc. biol.*, 1893, 586—590).—The experiments were carried out on dogs, and apocodeïne hydrochloride was injected hypodermically.

The heart is at first accelerated for a short period; the animal then becomes somnolent or sleeps, and the rate of the heart falls. This is entirely of central origin, and the course of the nervous impulses to the heart is by the pneumogastric nerves; the phenomena can be

prevented by section of these nerves. The blood pressure rises in the first and sinks in the second phase; the lowering of pressure is not, however, very great (not nearly as great as that produced by morphine), and is a result of the heart's slower action rather than of vaso-dilatation.

The rate of respiration runs parallel to that of the heart. The body temperature is lowered during the somnolent stage. The quantity of oxygen consumed and carbonic anhydride expired is also considerably lessened. The repose of the skeletal muscles and the slowing of the heart and respiration will partly explain these results ; but another factor is believed to be a lessening of inter-organic combustions. W. D. H.

Effects of Snake Venom. By C. J. MARTIN (*J. Physiol.*, **15**, 380—400).—The venom investigated was that of the Australian black snake (*Pseudechis porphyriacus*). The poisonous constituents are primary proteoses. The effect on the blood is principally dealt with in the present communication. The effect resembles that produced by injection of nucleo-albumin, sometimes producing intravascular coagulation, and sometimes, with larger doses, a condition of non-coagulability. On shed blood, a solution of the venom retards coagulation. The venom itself contains no nucleo-albumin. It probably acts by liberating nucleo albumin from the blood corpuscles. This view is supported by observations that show that the venom dissolves both kinds of blood corpuscles to some extent. The very minute doses necessary bear in the same direction. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Effect of Calcium Sulphite on Alcoholic Fermentation. By T. CHIAROMONTE (*Staz. Sper. Agrar.*, **23**, 360—379).—The hot climate of the south of Italy makes it difficult to obtain wines which will keep, the high temperature rendering a regular fermentation impossible. After enumerating the various proposed methods for keeping down the temperature of the must during fermentation, the author describes experiments on the action of calcium sulphite, which was shown by Czeppel to lower the temperature of fermenting liquids. Comparative experiments were made, both in a cellar and with smaller quantities in the laboratory, in which one quantity of must had no calcium sulphite added, and others were mixed with different amounts of the salt. The temperature was observed twice daily, and the amounts of alcohol produced each day ascertained. Sp. gr., total acid, and dry matter were also determined.

The following conclusions are drawn from the experimental results :—An addition of 5 to 10 grams of calcium sulphite per hectolitre does not lower the temperature of the fermenting liquid, but rather tends to stimulate the fermentation. A larger amount of sulphite

(20 to 30 grams) retards fermentation, whilst 100 grams per hectolitre stops it altogether. Biernaki has shown (*Arch. Physiol.*, **49**, 112) that many substances, mercuric chloride, copper sulphate, potassium permanganate, &c., when added in small quantities, accelerate fermentation (compare also Richet, *Compt. rend.*, **114**, 1494).

The stimulating action of calcium sulphite is greater, the larger the amount of ferment. It diminishes the acidity of the wine in proportion to the amount employed, owing to the liberation of the base.

The lime liberated from the sulphite neutralises more or less of the acid of the wine, and thus diminishes the already too low acidity of the southern wines; this can, however, be overcome by adding tartaric acid with the sulphite. Whilst the addition of calcium sulphite in sufficient amount to lower the temperature quite alters the character of the wine, smaller amounts induce more complete fermentation, but the advantage is too slight to make it worth while to employ the salt.   N. H. M.

Action of Alcohol and Sulphur on Yeast. By J. DE REY-PAILHADE (*Compt. rend. Soc. biol.*, 1893, 46—47).—Yeast was suspended in its own weight of water, and also in its own weight of alcohol, and the two were compared together. It was found that the alcohol killed the yeast and produced certain substances from the cells which have the power of decolorising (hydrogenising) indigo-carmine and litmus. It is, however, possible to produce the latter result without killing the organisms; this is accomplished by adding to the suspended yeast its own weight of sulphur; this leads to the evolution of hydrogen sulphide, which is then decomposed by the indigo-carmine.   W. D. H.

Beer Yeast. By J. EFFRONT (*Compt. rend.*, **117**, 559—561).— Experiments made with *Saccharomyces cerevisiæ* (*Pastorianus* 1, *Carlsberg*, and *Burton*), show that when yeast is cultivated in a sterilised malt wort containing 200—300 milligrams of alkali fluorides per litre, the power of propagation is reduced to an extent depending on the nature of the yeast. Worts of this kind can, however, serve for the cultivation of all varieties of beer yeast, provided that the latter have been habituated to the presence of fluorides by successive cultivations in solutions containing increasing quantities of fluorides.

The yeasts which have been cultivated in these liquids have a fermenting power very much greater than that of ordinary yeast. After five or six cultivations, this power may be increased as much as 10 times. Further, unlike ordinary yeasts, they can be employed successfully in distilleries without having first been passed through an acid leaven.   C. H. B.

Transformation of Starch into Sugar by the Bacillus anthracis. By MAUMUS (*Compt. rend. Soc. biol.*, 1893, 107—109).— The *Bacillus anthracis* was grown on potato. The surface of the potato then gave with iodine, not the blue of starch, but the red of dextrin. Other slices were then placed in sterilised water in flasks;

after two to six days at 37°, the liquid gave reduction with Fehling's solution. Later, however (six to seven days), all the sugar had disappeared, having possibly been used as a nutriment for the micro-organisms. W. D. H.

Influence of Metallic Salts on Lactic Fermentation. By A. CHASSEVANT and C. RICHET (*Compt. rend.*, **117**, 673—675).—The authors have determined the quantities of various metallic salts required to prevent the lactic fermentation of whey, a distinction being made between the quantity required to arrest reproduction and that necessary to stop fermentation, the former being called the *antigenetic dose* and the latter the *antibiotic dose*. The antigenetic dose varies from 0·5 gram molecule per litre, in the case of magnesium, to 0·000065 in the case of cobalt, the corresponding values for the antibiotic dose being 1·5 and 0·000065 respectively. The order of toxicity of the metals investigated is magnesium, lithium, calcium, strontium, barium, aluminium, manganese, iron, lead, zinc, copper, cadmium, platinum, mercury, nickel, gold, cobalt. In the case of magnesium and platinum, the antibiotic dose is three times as great as the antigenetic dose; in the case of mercury and cobalt, the two doses are identical; in other cases, the ratio varies from 2·5 to 1·2.

C. H. B.

Proteolytic Action of Bromelin. By R. H. CHITTENDEN (*J. Physiol.*, **15**, 249—310).—Bromelin, the ferment of pine-apple juice, appears to be associated with a peculiar proteose-like substance. In the present paper, attention is paid to the character of the isolated ferment and its action on the three typical proteids, fibrin, egg-albumin, and myosin. The resulting products (proteoses and peptones) were analysed, and full details are given of their properties and percentage composition. W. D. H.

Presence of Vegetable Trypsin in Fruit of Cucumis utilissimus. By J. R. GREEN (*Ann. Agron.*, **19**, 508—509.—Ferments which dissolve coagulated albumin are rare in the vegetable kingdom. To the few authentic cases (the pepsic ferment of the fruit of *Carica Papaya*, the papain of Würtz and of Vulpian, and the latex of the common fig tree) the author has added a pepsic ferment found in germinating lupin seeds, and now calls attention to one found in the fruit of *Cucumis utilissimus*, Roxb., a plant indigenous in India. The juice of this fruit dissolves boiled white of egg; the boiled juice has no such power. It does not depend on microbes, since the addition of thymol does not prevent the action. Salt water dissolves out more of the ferment than pure water. The author believes the ferment to belong to the globulins or allied bodies. Like papaïn, it resembles trypsin rather than pepsin, and is more active in presence of bases than in neutral or acid media; the products of its action on coagulated albumin are first peptone, afterwards leucine.

J. M. H. M.

Presence in Fungi of a Ferment analogous to Emulsin. By E. BOURQUELOT (*Compt. rend.*, **117**, 383—386).—23 species of fungi parasitic on living trees, or growing upon dead wood, contain a

soluble ferment, which has the power of decomposing glucosides, such as amygdalin, salicin, and coniferin, and it would seem to be through the medium of this ferment that the fungi are able to utilise as food the various glucosides present in the bark, cambium, and ligneous tissue of the trees or wood on which they live.

No similar ferment could be obtained from nine species of fungi growing upon the soil.

The ferment can be extracted in two ways. The freshly-gathered fungus is placed in an atmosphere saturated with the vapour of ether or chloroform, which causes an abundant exudation of a liquid containing the soluble substances of the cellular fluid. In the other method, the fungus is made into a paste by trituration with sand, and is then extracted with water.   C. H. B.

Formation of Saccharose during the Germination of Barley.

By L. LINDET (*Compt. rend.*, **117**, 668—670).—The finely-powdered barley was treated with alcohol of 91°, which dissolves the saccharose with only minute quantities of reducing sugars. After removal of acids by means of lead hydroxide, the rotatory power and reducing power were estimated, before and after inversion, by Clerget's process. 46 hours after the commencement of germination, the percentage of saccharose is 0·99, which, at the end of 70 hours, has increased to 1·85, and at the end of 94 hours to 2·20, and then very slowly increases until it becomes 3·09 at the end of 234 hours. Similar results are obtained on examining the infusions obtained by treating the barley with ice-cold water. The reducing sugars, like the saccharose, increase continuously during germination, from 2·72 per cent. to 6·28 per cent., the curves representing the increase of the saccharose and the reducing sugars being parallel.

The only substance that diminishes continually during the germination of the barley is starch, and this fact affords further support to the conclusion of Brown and Morris that, under certain conditions, saccharose is formed at the expense of starch.   C. H. B.

The Bleeding of Plants.

By A. WIELER (*Bied. Centr.*, **22**, 758—763; from Cohn's *Beitr. zur Biol. d. Pflanzen*, **6**).—In the present paper, the term bleeding is used not only to denote the secretion of sap from wounds, but also the secretion from leaves and from fungi, &c. At present, there are 439 varieties of plants known to be capable of bleeding; probably further investigations will show it to be a property of all plants, or, at least, all phanerogams. As regards the parts of plants which bleed, it occurs in all parts of the roots and most above-ground organs. Temperature plays an important part. Experiments in which young plants of *Hordeum vulgare* (which, like most *Gramineæ*, bleed at the points of the leaves) showed that when the surrounding air is replaced by an indifferent gas (hydrogen) the bleeding ceases, but begins again as soon as oxygen is admitted. This would indicate that bleeding depends on a direct process of oxidation. In presence of chloroform or nitrobenzene, the bleeding is more or less checked, so that it seems likely that changes which give rise to bleeding are not purely chemical.

Many plants show certain periods during which they bleed, with intermediate periods when no bleeding occurs. With other plants, the bleeding is almost continuous. Variations of the limits of the periods of bleeding occur with different plants of the same species. It is also possible, by the addition of certain compounds to the solution in which the plants are grown, to alter the bleeding period. Thus, glycerol (1—2 per cent.), cane sugar (5—10 per cent.), potassium and ammonium nitrates, sodium phosphate, magnesium sulphate, iron sulphate, hydrochloric and citric acids, methyl-violet (0·0001 per cent.), caffeine, $\frac{1}{2}$ per cent., and quinine hydrochloride ($\frac{1}{2}$ per cent.) are favourable to bleeding. Bleeding is also increased by exposure to a temperature of 37—39°; a temperature of 19—20° is insufficient, so that the commencement of bleeding in the spring cannot be caused by the increasing warmth. There seems to be no connection between bleeding and new root production. The author's experiments confirm Hofmeister's law, that the minimal bleeding is in the morning and the maximum in the afternoon. It is impossible, at present, to say whether the daily bleeding is induced by light.

N. H. M.

Production of Crystals of Calcium Oxalate in Vegetable Cell Membranes. By H. K. MÜLLER (*Bied. Centr.*, **22**, 786; from *Bot. Centr.*, 1892, 111).—The crystals are generally deposited within the membrane without contact with the cell-contents, but are sometimes formed inside the cells, and subsequently gradually enclosed in the membrane. The question as to the chemical process involved in the production of the crystals remains undecided, but it seems likely that they are formed by the contact of a soluble oxalate and a calcium salt in the membrane.

N. H. M.

Calcium Oxalate in Plants. By H. WARLICH (*Bied. Centr.*, **22**, 786—787; from *Bot. Centr.*, 1892, 113).—Deposition of calcium oxalate occurs during the growth of leaves, and probably, also, when the leaves have ceased to grow. Oxalic acid is the solvent. In experiments with *Vanilla planifolia*, it was found that Wakker's "elaioplasten" became doubly refractive as they become older, and that at this period there are no crystals present. After treatment with dilute sulphuric acid, they are no longer doubly refractive. With increasing age, the crystals form from cell to cell, until, in still older leaves, they are generally close together, and at last the "elaioplast" disappears.

Calcium oxalate is sometimes redissolved in the plant.

N. H. M.

Amount of Ethereal Thiocarbimides obtained from Rape Cake. By ULBRICHT (*Bied. Centr.*, **22**, 732—733).—The thiocarbimides found in rape cakes are due not only to the seeds of foreign *Cruciferæ*, but also to home-growing plants; if cakes contain more than 0·5 per cent. of the oil, it should only be given in the dry state, and even then, not to pregnant or milking animals.

Rape seed itself contains only one-half, and even less, oil than is contained in the cake, and this is believed to be due to the heating at 70° necessitated by the process of manufacture.

E. W. P.

Indian Water-chestnut. By D. HOOPER (*Pharm. J. Trans.*, **53**, 22—23).—The Indian water-chestnut (*Trapa bispinosa*), an aquatic plant extensively cultivated in the North-West Provinces of India, yields nuts whose white kernels are roasted and pounded to a flour, which is largely used as a food. The author's analysis of the powdered kernels gave the following results in 100 parts :—fat, 0·97 ; sugar and gum, 14·36 ; albuminous matter, 8·41 ; starch, 63·84 ; cellulose, 3·60 ; ash, 4·66 ; water, 4·16. The substance contained 1·33 per cent. of nitrogen, and the "nutrient-ratio," that is, the ratio of albuminous to starchy matters, was 1 : 9·5 ; the nutrient value, 80·4. It is, therefore, as a food, comparable with the cereals, and is better than cleaned rice, which has the nutrient ratio of 1 : 10·8. The *Trapas* have been noted for their power of taking up manganese ; thus Gorup-Besanez found 1·61 per cent. of manganese oxide in the whole plant of *Trapa natans*. The author found in the above-mentioned 4·66 per cent. of ash from the edible portion, only a very small quantity of manganese, but the pericarp was very rich in that metal.   R. R.

Composition of Russian Barley. By V. TISHTCHENKO (*J. Russ. Chem. Soc.*, **25**, 163—169).—The author has compiled, from his own observations and other data, a table giving the amount of proteïd matter (nitrogen × 6·25) in 62 samples of barley grown in different districts of Russia and used for brewing purposes. In some cases, the moisture, starch, ash, and phosphoric acid are also given. He finds that the nitrogen of crops grown in the same district in different years is fairly constant, and that three characteristic types may be distinguished. Polish barley contains·10—11 per cent. of albuminous matter ; Tzaritzinsk (Don district), barley, 15 per cent. ; and Tcherimiss (upper Volga and Kama), barley, 12 per cent. ; the mean percentage for barley grown in Western Europe being from 10·5 to 11·5.   J. W.

Analytical Chemistry.

Detection of Chlorine, Bromine, and Iodine in the same Mixture. By J. TORREY (*J. Anal. and Appl. Chem.* **6**, 667—669).— The author has slightly modified the process originated by Hart and communicated by Kebler. The bulb tube arrangement has been replaced by a small tube having only one small bulb blown on it, the tube being bent slightly away from the perpendicular about half an inch above where it leaves the cork. Above the bulb there should be about half an inch of tube left. The flask containing the mixture is charged with ferric sulphate as usual, and the iodine evolved is readily detected by holding in the steam a small piece of starch-paper. When iodine fumes can no longer be detected, a crystal of potassium permanganate is added, and, on further heating, bromine

is given off, which is best detected by allowing the fumes to act on iodised starch paper. The boiling must be quite brisk, or else the bromine will not be completely expelled. The residue is then tested for chlorine in the usual manner. The author advises working on a very small quantity of substance. L. DE K.

Titration of Caustic Liquors containing Chlorine. By C. ULLMANN (*Chem. Zeit.*, **17**, 1208—1209).—A measured quantity of the lye is mixed with an excess of standard solution of succinic acid and heated until the odour of hypochlorous acid has gone off. The excess of acid is then titrated with standard soda, using phenolphthaleïn as indicator.

Succinic acid expels carbonic anhydride and hypochlorous acid, but is without action on chlorides, and is also proof against oxidising or chlorinating agents. L. DE K.

Estimation of Nitrogen in Manures containing Nitrates. By V. SCHENKE (*Chem. Zeit.*, **17**, 977—979).—After reviewing a large number of processes, the author finally recommends the following, which is really a combination of Kjeldahl and Ulsch's processes. A few grams of the sample is introduced into a 300 c.c. flask, and treated with about 4 grams of reduced iron and some 10 c.c. of dilute sulphuric acid (1—2). After applying a gentle heat to complete the reduction, a sufficiency of sulphuric acid containing 20 per cent. of phosphoric anhydride is added, and also a little copper oxide. The mixture is now further treated as in Kjeldahl's process. L. DE K.

Reaction of Hydroxylamine. By A. ANGELI (*Gazzetta*, **23**, ii, 102).—A new reaction for hydroxylamine consists in adding to its neutral aqueous solution first sodium nitroprusside, then caustic soda; on boiling the mixture, it becomes coloured a fine magenta red. The red colour produced by phenylhydrazine under similar conditions disappears on heating. The test is very sensitive, but should not be applied to solutions containing a large excess of ammonium salts. W. J. P.

Estimation of Yellow Phosphorus. By G. TÓTH (*Chem. Zeit.*, **17**, 1244—1245).—The phosphorus is dissolved in carbon bisulphide, and the solution is diluted with olive oil and agitated with solution of silver nitrate. The argentic phosphide thus obtained is oxidised by means of dilute nitric acid, and the aqueous layer is separated from the oil.

The phosphoric acid is now estimated by the molybdate method and calculated to phosphorus. In four test experiments, 78, 93, 93 and 100 per cent. of phosphorus was respectively recovered. L. DE K.

Estimation of Sulphur in Steel, Iron, &c. By H. A. HOOPER (*Chem. News*, **68**, 191).—The steel or iron is dissolved in hydrochloric acid, and the sulphur, evolved as hydrogen sulphide, is absorbed in caustic soda and subsequently titrated with a standardised solu-

tion of lead nitrate. Rapidity and delicacy are claimed for the
method. D. A. L.

Volumetric Estimation of Lead. By A. P. LAURIE (*Chem.
News*, **68**, 211).—To estimate lead in the presence of hydrochloric
acid, it is directed to neutralise the acid, add sodium acetate, avoiding
large quantities of other salts, then to titrate with standardised
potassium dichromate, made up to precipitate 0·002 gram of lead per
c.c., using silver nitrate as indicator, a yellow tint in the precipitate of
silver chloride indicating the end of the reaction. The sensitiveness
is influenced by the proportion of chloride present, the most satisfac-
tory amount being from 0·5 to 0·2 gram of sodium chloride in
100 c.c. To obviate inconvenience, arising from the formation of
basic salts and from floating particles of lead chromate, most of the
required quantity of dichromate is added at once, and the liquid is
gradually heated to boiling with frequent stirring. D. A. L.

Assay of Copper Sulphate. By J. RUFFLE (*Analyst*, **18**, 279—
281).—The author estimates the copper electrolytically, and calculates
it into the crystallised sulphate. This, on being heated at 100° to
constant weight, loses 28·91 per cent. of water. If now a sample
loses more water than corresponds with the copper sulphate it con-
tains, the excess may be put down to adherent moisture.

For the pupose of estimating any free sulphuric acid, 20—50 grams
of the sample is powdered and repeatedly extracted with absolute
alcohol. The alcoholic filtrate is diluted with water, mixed with a
few drops of phenolphthaleïn, and titrated with standard soda.
L. DE K.

Separation of Copper from Cadmium by the Iodide Method.
By P. E. BROWNING (*Amer. J. Sci..* [3], **46**, 280—283).—The author
recommends the following modification of the iodide process. The
solution containing the two metals is mixed with potassium iodide as
long as a precipitate forms, and the liberated iodine is boiled off.
The cuprous iodide is collected on a weighed asbestos filter, washed,
dried at 120—150°, and weighed. The filtrate is heated with potas-
sium nitrite and sulphuric acid to decompose the excess of iodide, and
when every trace of iodine is expelled, the cadmium is precipitated
by boiling with sodium carbonate. The cadmium carbonate is next
collected on an asbestos filter, and converted into oxide by ignition.
The test analyses are extremely satisfactory. L. DE K.

Quantitative Analysis by Electrolysis. By A. CLASSEN (*Zeit.
anorg. Chem.*, **5**, 231—236).—A rejoinder to Rüdorff (Abstr., 1893,
ii, 391).

Effect of Platinum in Iron Solutions. By R. W. MAHON (*Amer.
Chem. J.*, **15**, 578—582).—When the insoluble residue of an iron ore
is fused with sodium carbonate in a platinum crucible, and the melt
dissolved in hydrochloric acid, some platinum, usually about 1 milli-
gram, goes into solution, and this affects the estimation of the iron
with standard dichromate, in the case when the iron is reduced to the

ferric state by means of stannous chloride, the excess of the latter being removed with mercuric chloride. The platinum chloride functions continuously, undergoing a cycle of changes the net result of which is to oxidise the ferrous to ferric chloride at the expense of mercuric chloride, which is reduced to mercurous chloride. The error introduced may thus be large; it is increased by protracted fusion, by the presence of much free hydrochloric acid, or by the addition of a large excess of stannous chloride. It may be made small by avoiding these conditions; but, to ensure an accurate result, it is best to free the iron from platinum by precipitating it with ammonia, and redissolving the washed precipitate in hydrochloric acid.   C. F. B.

Estimation of Ferric Oxide and Alumina in Mineral Phosphates. By G. MARIANI and E. TASSELLI (*Staz. Sper. Agrar.*, 23, 31—37).—The method of estimating ferric oxide and alumina by precipitating the phosphates with ammonia and acetic acid has been almost entirely superseded by Glaser's method (Abstr., 1890, 420), on account of the partial precipitation of lime and the partial solubility of the phosphates in the acetic acid. Another cause of error which seems to have been overlooked is the sparing solubility of ferric orthophosphate in hot water (Sestini, *Staz. Sper. Agrar.*, 1875). The following modification is recommended as giving accurate and concordant results as shown by experiments with solutions of known strength. Glaser's method gave somewhat lower results except with basic slag; in this case, however, the results were higher, owing to the presence of manganese, which is liable to be precipitated with the iron and aluminium.

The phosphate (1—5 grams) is boiled with hydrochloric acid (15 c.c.) for about 10 minutes, diluted with water (2 parts), and oxidised by means of crystals of potassium chlorate and a few drops of nitric acid, the whole being boiled to expel most of the chlorine. It is then filtered, washed, the filtrate made up to about 150 c.c., and a solution of ammonium phosphate (0·5 gram) added, then glacial acetic acid (2 c.c.) and, drop by drop, ammonia until a slight permanent precipitate is produced, after which slightly ammoniacal water is gradually added until a slightly alkaline reaction is obtained; acetic acid (2 c.c.) is now added, the whole shaken, and left for two hours. The clear liquid is decanted through a filter, the precipitate being washed with a 1 per cent. solution of ammonium phosphate; the funnel containing the precipitate is put over the same flask, and the precipitate redissolved by pouring on, drop by drop, hydrochloric acid (sp. gr. 1·12). After washing the filter sufficiently, the iron and alumina are again precipitated as before, then left for an hour, decanted through a filter, washed with ammonium phosphate solution, dried, ignited (with filter) at a dull red heat, and weighed.

This modification gives as good or better results than Glaser's, but it may be possible to improve the method still further.

N. H. M.

Estimation of Chromium in Ferrochrome. By J. Spüller and S. Kalman (*Chem. Zeit.*, **880**, 1207—1208).—The authors mix 0·35 gram of the finely-powdered substance with 8 grams of sodium hydroxide and 4 grams of sodium peroxide, and ignite for about an hour in a silver dish with occasional stirring. After cooling, the mass is dissolved in water, and any sodium ferrate or manganate decomposed by adding more sodium peroxide ; the excess of the latter being removed by passing a current of carbonic anhydride, and gently warming. The chromate is then estimated by means of a ferrous salt according to Schwarz's method.   L. DE K.

Assay of Tin Ores. By H. W. Rennie and W. H. Derrick (*J. Soc. Chem. Ind.*, **11**, 662—667).—The ore is pulverised until it will pass through a sieve of 60 meshes, or for low grade ores containing much iron one of 90 meshes, to the linear inch ; 250 grains of it is then boiled for half an hour with 3 oz. of hydrochloric acid and $\frac{1}{2}$ oz. of nitric acid, and the residue carefully washed by decantation ; wolfram, if present, may be dissolved out by ammonia. The residue is then washed on a vanning shovel, when, by skilful manipulation, the free silica can be washed away without the loss of a trace of tin, leaving nearly pure cassiterite. In many cases the percentage of cleaned cassiterite furnishes sufficient information, but when it is required to know the actual percentage of tin, 50 grains of this oxide is reduced by potassium cyanide with the following precautions. The cyanide should be pure and finely powdered, and both it and all the apparatus should be thoroughly dry ; crucibles about 3 in. high, of a fine-grained clay and of a smooth interior, should be used, otherwise numerous minute prills of tin adhere to the crucible and cannot be collected. A layer of cyanide is first rammed into the crucible, then the mixture of oxide with 300 grains of cyanide, and finally a covering of cyanide. The crucible, closely covered, is then placed in a muffle, already at a low red heat that the cyanide may fuse rapidly, but not froth. After 10 minutes, the crucible is gently shaken to wash down prills from the sides ; the heat is then raised to a bright red for another five minutes. The traces of silica present form a globule of greenish slag, less fusible than the cyanide. As the temperature is raised, this detaches itself from the metal and rises to the surface. As soon as this has occurred, the crucible is allowed to cool, and its contents treated with boiling water, when the button of metal is left in a state fit for weighing. The results leave nothing to be desired in point of accuracy.   M J. S.

Separation of Copper from Bismuth. By E. F. Smith (*Zeit. anorg. Chem.*, **5**, 197—198).—A rejoinder to Classen (Abstr., 1893, i, 495).

Separation of Copper from Bismuth. By A. Classen (*Zeit. anorg. Chem.*, **5**, 299).—A reply to Smith, who has pointed out an error in the author's work on electrochemical analysis.

Quantitative Separation of Metals in Alkaline Solution by means of Hydrogen Peroxide. By P. JANNASCH and J. LESINSKY (*Ber.*, **26**, 2908—2912; compare this vol., ii, 32).—*Separation of Bismuth from Copper.*—Bismuth and copper (about 0·3 gram of each) are dissolved in concentrated nitric acid (5 c.c.), diluted with water (50 c.c.), and the bismuth precipitated by means of a mixture of 3 per cent. hydrogen peroxide (50 c.c.) and concentrated ammonia (15 c.c.), care being taken to avoid loss by frothing. The precipitate is washed first with a mixture of hydrogen peroxide (2 vols.), concentrated ammonia (1 vol.), and water (8 vols.), secondly with warm dilute ammonia (1 : 8), and finally with hot water; the complete removal of the copper is attained with difficulty. The bismuth oxide is dried at 90—95°, ignited with the filter paper in a platinum dish, and the residue dissolved in nitric acid, and ignited until its weight is constant. The copper, after conversion into sulphate and removal of the nitric acid, is precipitated by the prolonged action of hydrogen sulphide, and the precipitate converted into oxide by ignition in a stream of oxygen. The analytical results show that the amount of bismuth obtained is in excess of the theoretical by 0·2—0·3 per cent. Heating the liquid immediately after the precipitation of the bismuth appears to be without marked result, except that traces of copper are retained by the bismuth oxide, and can only be removed by redissolving it and re-precipitating. The addition of hydroxylamine (Abstr., 1893, ii, 500) is attended by a similar result, the bismuth oxide being deposited as a white, crystalline powder.　　　　J. B. T.

Estimation of Gold and Silver in Antimony or Bismuth. By E. A. SMITH (*J. Soc. Chem. Ind.*, **12**, 316—319).—*Assay of Antimony for Gold and Silver.* *1st Method.*—The sample is powdered in an iron mortar, passed through a sieve of 80 holes to the linear inch, and well mixed. 500 grains of the powder is then mixed with 3000 grains of litharge, put into an earthen crucible, and fused in an air furnace, the crucible being partly covered during the operation, which lasts about 15 minutes. The melt is poured into an ingot, and, after cooling, detached from the slag. The lead button, although a little hard, is malleable, and, after being scorified to a convenient size, it may be cupelled in the ordinary way. The gold is afterwards parted from the silver by means of nitric acid. When assaying samples fairly rich in gold or silver, small quantities of the precious metals may be retained by the slag. The latter should therefore be again fused with 500 grains of litharge and 20 grains of charcoal, and the lead button thus obtained cupelled as before.

2nd Method.—500 grains of the sample of antimony is fused with 1000 grains of litharge, 200 grains of nitre, and 200 grains of sodium carbonate. The fusion is generally complete in 15 minutes, and the buttons of lead may be at once cupelled without previous scorification, thus saving considerable time. The test analyses are satisfactory.

Assay of Bismuth.—The metal is melted under a layer of charcoal, and, after adding a piece of resin, it is poured into moulds so as to

obtain buttons weighing about 500 grains. After adjusting them to exactly 500 grains, they are at once carefully cupelled in a muffle at a slightly lower temperature than that employed for the cupellation of lead. The resulting buttons of gold and silver are then treated as before with dilute nitric acid.   L. DE K.

Sodium Peroxide in Water Analysis. By S. RIDEAL and H. J. BULT (*Chem. News*, **68**, 190—191).—It is found that on treating potable water, or water contaminated with fresh sewage, with sodium peroxide (in a solution containing 2 grams per litre) instead of with alkaline permanganate, only part of the organic matter is attacked, and, consequently, after such treatment, the waters yield a further quantity of ammonia with permanganate; this residual organic matter is, however, much more readily oxidised than the organic matter that has not been treated with the peroxide.   D. A. L.

Amount of Glucose in Beets and in Diffusion Juice. By H. CLAASSEN (*Bied. Centr.*, **22**, 769—771).—The percentage of glucose present in beet-root should be estimated in the root itself and not in the expressed juice.

Slices of the root are digested in water, basic lead acetate is added (not in excess), and the whole further digested; the solution is then neutralised by calcium carbonate, in order that there may be no free alkali. After filtration, the lead is precipitated by soda, and the sugar present estimated by means of Fehling's solution.

                                                        E. W. P.

Estimation of Glycogen. By J. WEIDENBAUM (*Pflüger's Archiv*, **54**, 319—332).—The research consisted in a critical investigation of Fränkel's method of separating and estimating glycogen (Abstr., 1893, i, 386).

The glycogen obtained by this method is very impure; dissolved in dilute potash, it gives, after neutralisation with hydrochloric acid, a fairly heavy precipitate with Brücke's reagent. The longer the organ is treated with trichloracetic acid, the greater is the nitrogen present in the so-called glycogen extracted; in some cases, almost half the substance is proteïd. The residue, also, is not freed from glycogen by the extraction, nearly a third of the total glycogen being left behind.   W. D. H.

Colour Reaction of Phenylhydrazine on Lignin and Aldehydes. By E. NICKEL (*Chem. Zeit.*, **17**, 1209, 1243—1244).—Wood, immersed in a solution of phenylhydrazine hydrochloride, turns pale yellow, the colour deepening on the addition of dilute hydrochloric acid. After the lapse of an hour, or sometimes several hours, the colour changes to a distinct green. Wood, and particularly bamboo, immersed in a solution of hydrazine sulphate, acquires, after a few minutes, a clear yellow colour, which turns orange on adding hydrochloric acid.

Hydrazine sulphate, added to a solution of vanillin, produces a deep yellow coloration, but no precipitate; the addition of hydrochloric acid gives a flocculent, yellow precipitate, but this did not turn orange.

Piperonal, parahydroxybenzylaldehyde, and salicylaldehyde give similar colorations. L. DE K.

Estimation of Oxalic acid. By A. GUNN (*Pharm. J. Trans.*, **53**, 408—410).—The author proposes to use the yellow colour of ferrous oxalate as a means of determining oxalic acid in certain cases where the ordinary methods are not readily applicable. Absolute accuracy is not claimed for the process, but it appears to be specially useful for estimating oxalic acid when mixed with tartaric acid. The solution of ferrous salt preferred is that of the phosphate, which is nearly colourless, and the determination is made colorimetrically by comparison in Nessler glasses with a standard solution. The colour is destroyed by the strong mineral acids, and the reaction is also interfered with by the presence of much alum. The results are improved by a preliminary neutralisation of the acids by ammonia. Coloured solutions may be first treated with animal charcoal, and any residual tint allowed for in the comparison. R. R.

Estimation of Tannin and Gallic acid. By W. P. DREAPER (*J. Soc. Chem. Ind.*, **12**, 412—415).—The author recommends the following process. The solution containing the tannin and gallic acid is heated to 80°, and, after adding some pure barium carbonate, a standard solution of copper sulphate is added until a drop of the supernatant liquid gives a faint brown coloration when mixed with potassium ferrocyanide. Another portion of the solution is precipitated by means of gelatin, and, after filtering, the titration is repeated. The difference in c.c. of copper solution between the two estimations is the measure for the amount of tannin. The copper solution should, of course, be checked with pure tannin and also with gallic acid, as the latter requires a much larger amount of copper for precipitation than tannin does. L. DE K.

Analysis of Tanning Materials. By A. GAWALOWSKY (*Zeit. anal. Chem.*, **32**, 618—619 ; from *Brestewski's Handworterbuch für Pharmacie*).—An extract of the material is precipitated with the smallest possible excess of copper acetate, and after a time is filtered by suction through a dried and weighed filter ; the precipitate is washed with cold water, dried until the weight is constant, and incinerated. The ash is dissolved in nitric acid and again ignited to determine the copper as oxide. The difference gives the total tannin, gallic acid, pectin, &c. Another part of the extract is evaporated to a syrup, treated with alcohol-ether (2 : 1), and the pectin with traces of albumin and casein filtered off ; the alcohol-ether is evaporated from the filtrate, and the residue dissolved in hot water and filtered from fat and resin. The cold filtrate is now mixed with copper acetate and ammonium hydrogen carbonate ; this precipitates the tannin, leaving copper gallate in solution. The pectin precipitate is dissolved from the filter with hot water, and the cooled solution precipitated with copper acetate. Both these precipitates are treated like the former one ; the gallic acid is then known from the difference. M. J. S.

Separation of Uric acid from Xanthine. By J. HORBACZEWSKI (*Zeit. physiol. Chem.*, **18**, 341—350).—In view of a certain amount of hostile criticism which has followed the publication of the author's views on the origin of uric acid in the organism from nuclein, he admits that the separation of uric acid from xanthine bases is difficult. Artificial mixtures of uric acid and xanthine showed a loss of uric acid when that substance was estimated by Fokker's method. The separation of the two substances by means of hydrochloric acid led to better results; but there is still a noteworthy loss. By means of concentrated sulphuric acid, the mixture being allowed to stand five hours, the loss is inconsiderable, the greatest difference being 0·005 gram. If longer than five hours is allowed to elapse, some xanthine is precipitated also.

The same method was successfully carried out in the separation of uric acid from guanine.   W. D. H.

Precipitability of Uric acid and Bases of the Uric acid Group as Cuprous Oxide Compounds. By M. KRÜGER (*Zeit. physiol. Chem.*, **18**, 351—357).—By the use of copper sulphate and sodium hydrogen sulphite, all xanthine-like substances which contain a substituted NH-group are precipitated from hot solutions as compounds with cuprous oxide. Theobromine is a noteworthy exception. As a quantitative method, it is as good as ammoniacal silver solution. The use of sodium thiosulphate as a reducing agent gives a means of separating adenine and hypoxanthine, and probably also of guanine and xanthine.   W. D. H.

Assay of Naphtholsulphonic and Naphthylaminesulphonic acids. By W. VAUBEL (*Chem. Zeit.*, **17**, 1265—1266).—The sulphonic acids may be divided into three classes :—1. Those which generally absorb only 1 atom of bromine; 2. Those which slowly absorb several atoms of bromine; 3. Those which do not combine with bromine at all. Only those of the first class can be readily assayed by the author's process. They comprise : *a*, naphthionic acid; *b*, Dahl's disulphonic acid II ; *c*, Dahl's disulphonic acid III ; *d*, para-monosulphonic acid (2Br) ; *e*, naphthylenediaminemonosulphonic acid.

The analysis is carried out by dissolving a known weight of the compound in water, and adding excess of potassium bromide and dilute sulphuric acid. Standard solution of potassium bromate is then added from the burette until the liquid contains free bromine.
                                                     L. DE K.

Hübl's Iodine Absorption Process. By W. FAHRION (*Chem. Zeit.*, **17**, 1100).—The author (Abstr., 1893, ii, 103) has demonstrated that the action of Hübl's reagent on oils is not quite so simple as has been supposed, and that iodine is also absorbed by other fatty constituents. In this view, the author is supported by Gantter, who has found that even saturated fatty acids combine with iodine.

The author has tried to improve the process by substituting methylic alcohol for ethylic alcohol in preparing the reagent, but,

excepting the fact that the solution keeps better, no special advantage accrues therefrom. L. DE K.

Reducing Action of Rancid Fat and Lard on Silver Nitrate. By G. MARIANI (*Staz. Sper. Agrar.*, **23**, 355—359).—Experiments were made with Brullé's nitrate of silver test for margarine (Abstr., 1891, 506). Pure butter gave no colour, and pure margarine did not give the red colour mentioned by Brullé. But in presence either of rancid butter or rancid margarine there was either a blackish deposit or a mirror, according to the degree of rancidity. Fresh hog's fat, on the other hand, reduced the silver salt, acquired a more or less intense red colour, and formed a brownish deposit.

An examination of the deposits obtained on the one hand from rancid butter and margarine, and from fresh lard on the other, showed that, whilst the former consisted of silver oxide and silver, the latter contained sulphide as well as oxide of silver. It is thus seen that lard, like the oils of some Cruciferæ, contains sulphur. In confirmation of this it was found that Benedikt's reaction for colza (*Anal. d. Fette*, 227) is also shown by lard.

The reaction is thus useless for the detection of margarine in butter. N. H. M.

Pennetier's Method for detecting Margarine in Butter. By A. PIZZI (*Staz. Sper. Agrar.*, **22**, 131—137, and **23**, 35—43).—Several examinations, by Pennetier's microscope-polariscope method, of pure butter and butter mixed with various amounts of margarine were made, the results of which are shown in a coloured plate. An examination was also made of the fat of natural butter, which was obtained by melting the butter, allowing it to partially solidify, and separating the solid portion; this, when examined with the polariscope, showed a red ground with detached yellowish and greenish particles, whilst ordinary butter shows a red ground mostly covered with a confused mass of various colours.

Some of the objections to Pennetier's method are the difficulties introduced by conditions of temperature, the effect of added crystalline and amorphous substances, and the manner in which the margarine may have been mixed with the butter. As regards the first, the author observed no difference between butter which had been melted and cooled quickly and butter which had been slowly cooled. With butter containing margarine which had been kneaded in, the method, gives good results, but when churned with the butter the mixture behaved like pure butter.

Very rancid and mouldy butter gave the margarine reaction. The inner portions of rancid butter, which had no mould on the surface, gave a negative optical reaction, whilst the outer portions gave a positive reaction. L. DE K.

The method will show the presence of margarine, but is limited in its application. N. H. M.

Estimation of Nicotine in Tobacco. By R. KISSLING (*Zeit. anal. Chem.*, **32**, 567—571).—The author vindicates his method against the strictures of Vedródi (Abstr., 1893, ii, 504), and asserts

that if his instructions are accurately followed, the ethereal extract will contain no ammonia, that no nicotine will be lost during the distillation of the ether, and that the results of his method agree closely with those of Popovici (Abstr., 1889, 802). The extraction with ether should, however, follow as quickly as possible the addition of the soda to the tobacco, as otherwise a loss of nicotine may take place.   M. J. S.

Furfuraldehyde Reactions of Alkaloïds. By N. WENDER (*Chem. Zeit.*, **17**, 950—951).—When two or three drops of a mixture of sulphuric acid and furfuraldehyde (5 drops to 10 c.c. acid) is added to a minute particle of an alkaloïd, a characteristic colour makes its appearance, and the author has tabulated the results. The method is, however, only of distinct value in the case of veratrine. This, when rubbed with a glass rod moistened with the reagent, gives first a yellowish-green, and then an olive-green mixture; the edges, and the whole of the mixture afterwards, turn a beautiful blue. On warming, the mixture gradually acquires a purple-violet colour. The blue substance obtained in the cold is insoluble in alcohol, ether, or chloroform. The least amount of water, or alkali, decolorises the solution, and on adding much water a fairly permanent yellow solution is obtained.

Excepting sabadilline, no other alkaloïd gives the reaction, although the test with that alkaloïd is not quite so satisfactory. If instead of sulphuric acid other acids are used, the reaction does not manifest itself.   L. DE K.

Estimation of Nitrogen and Proteïds in Milk and its Products. By L. CARCANO (*Staz. Sper. Agrar.*, **22**, 261—263).—According to L'Hôte (Abstr., 1889, 438 and 746), and Oddy and Cohen (Abstr., 1890, 1466), Kjeldahl's, method is not suitable for certain substances; with some, it gives coloured solutions after prolonged heating, and low results are obtained owing to incomplete oxidation, and to loss of ammonium sulphate during the heating. Menozzi, and also Musso (*Gazzetta*, **6**), estimated nitrogen in milk and its products by Dumas', and by Will and Varrentrapp's methods; they both found that the Will and Varrentrapp method gave low results (compare also Violette, Abstr., 1889, 546, and Aubin and Alla, *ibid.*, 648 and 925).

The author estimated the nitrogen in milk, Emmenthaler cheese, and cheeses prepared from mare's milk and from sheep's milk, &c., employing both Dumas' and Kjeldahl's methods. Proteïds were also determined in milk by Ritthausen's method. The modification of the Kjeldahl process was that recommended by the Directors of the Italian Agricultural Stations, with due regard to precautions mentioned by Zecchini and Vigna (Abstr., 1889, 649), and by Proskauer and Zülzer (*Chem. Centr.*, 1885, 17). In every case except one, the Kjeldahl results were somewhat lower than those obtained by Dumas' method, but the difference was generally very slight.

For milk analysis, the Kjeldahl process is much less troublesome than Dumas' method, and, although somewhat slow, several determinations can be carried on at once.   N. H. M.

General and Physical Chemistry.

Observations on Optical Rotation. By J. A. LE BEL (*Bull. Soc. Chim.*, [3], **9**, 674—680).—The experiments recorded in this paper were made to throw light on the law of the change of sign when the radicles of optically active compounds are replaced by others, notably by acidyl groups and halogen atoms. The author enters at length into his own theoretical views and those of Guye. His conclusions are not definite, but he states that the optical action appears to increase with the mass (Guye's hypothesis).

Methylpropylcarbinol is prepared by the hydrogenation of the mixed ketone obtained by distilling calcium acetopropionate. After growing *Penicillium glaucum* in its solution, it becomes lævorotatory; the chloride is slightly dextrorotatory, and the iodide more so. The tartaric chlorhydrins, methylpropylcarbinol and its derivatives, as well as ethylpropylcarbinol, were examined. The iodide from the last compound is lævorotatory, not dextrorotatory, as stated (Abstr., 1893, i, 246). Derivatives of methylamylcarbinol, propylglycol, the ethereal lactates, and isobutylamyl ether were also examined.   A. R. L.

Electromagnetic Rotation of the Plane of Polarisation of some Acids and Salts in different Solvents. By O. HUMBURG (*Zeit. physikal. Chem.*, **12**, 401—415).—In order to ascertain whether a connection exists between the magnetic rotation of an electrolyte and its electrolytic dissociation, a number of fatty acids and of inorganic salts were examined in solution in water and in other solvents. Benzene and toluene were used as solvents for the fatty acids, and methylic alcohol for the salts examined. The rotation of the fatty acids is independent of the solvent, and is the same in aqueous solution, in benzene, and in toluene; this holds even in the case of the chloracetic acids, which must be regarded as strongly dissociated in aqueous solution. The inorganic salts taken were potassium iodide, sodium and barium bromides, and ammonium nitrate. The molecular conductivities of these salts is much smaller when measured in the methylic alcohol solutions than in water, and, therefore, as was to be supposed, the dissociation is relatively much smaller in the first case. The rotation, however, remains practically unchanged with change of solvent, showing that it is independent of the dissociation. From the results of these experiments, therefore, it appears that electrolytic dissociation has no appreciable influence on the magnetic rotation.

The rotations of chlorine and bromine derivatives of some of the fatty acids and of some hydrocarbons were measured, and from these the atomic rotations of chlorine and bromine were calculated. The numbers obtained were, for chlorine 1·606 in the case of the fatty acid derivatives, and 1·675 from hydrocarbon derivatives; for bromine, 3·525 and 3·563 in corresponding cases. The numbers are practically identical in the two series.   H. C.

Optical Rotation and Electrolytic Dissociation. By H. HÄDRICH (*Zeit. physikal. Chem.*, **12**, 476—497).—According to Oudemans, the molecular rotation of salts in dilute solution is independent of the character of the inactive ion of the salt, a result which is in full accordance with the electrolytic dissociation theory. This view has been called in question, notably by Frankland (Trans., 1893, 312), and in this paper the author submits it to further experimental investigation. The salts examined were, in the first instance, those of the alkaloïds morphine, quinine, conquinine, cinchonidine, brucine, and strychnine. In each case in sufficiently dilute solution, the rotation is found to be independent of the inactive acid, and, therefore, the same for the different salts of any one alkaloïd. This is also true of the methylammonium salts of the alkaloïds. In these cases, therefore, the law of Oudemans is fully confirmed. Boryl, arsenyl, and antimonyl tartrates were also examined, and these in dilute solution are found to obey Oudemans' law. The rotation of these salts differs from that of the other tartrates, and therefore the active ion is not that present in tartaric acid itself.   H. C.

Reverberatory Electrical Furnace with Movable Electrodes. By H. MOISSAN (*Compt. rend.*, **117**, 679—682).—The furnace consists of a parallelopiped of Courson limestone, in which is cut a somewhat large cavity, also a parallelopiped in shape, which is lined with alternate plates of magnesia and carbon, about 10 mm. thick, so arranged that magnesia is in contact with the limestone, whilst carbon forms the internal lining of the cavity. A lid, of alternate plates of magnesia and carbon, covers the cavity, and a block of Courson limestone is placed above this lid. The electrodes are movable, and pass through slots cut in opposite sides of the furnace. At right angles to the electrodes a carbon tube, 10 to 20 mm. in diameter, passes through the furnace, and is so arranged as to be 10 mm. below the arc, and 10 mm. above the bottom of the cavity. If necessary, the tube can be lined with magnesia. By inclining the tube at an angle of about 30°, the furnace can be made to work continuously, the reducible material being introduced at the higher end, whilst the product of reduction is drawn off at the lower end. With a current of 600 ampères and 60 volts, 2 kilos. of fused metallic chromium can be obtained in about an hour, the metal being received in a crucible made of chromic oxide. The metal is white, finely granular, and very hard, and takes a high polish.

The magnesia is prepared by heating strongly the basic carbonate, digesting the product with ammonium carbonate solution, and again strongly heating. It is then moistened with water and compressed.

With this furnace, silicon carbide and vanadium carbide can be readily obtained by the direct combination of carbon vapour with the vapours of silicon and vanadium.   C. H. B.

Electrolytic Thermoelectric Cells. By A. GOCKEL (*Ann. Phys. Chem.*, [2], **50**, 696—704).—The author has investigated the electromotive force of thermo-elements constructed on the following plan :

Hg | solid Hg salt : salt solution : solid Hg salt | Hg

$$\frac{\qquad\qquad}{\text{cold}\qquad\qquad\qquad|\qquad\qquad\text{hot}}$$

He finds that in general the thermoelectric force for 1° difference of temperature increases with dilution of the solution, and that in equivalent dilute solutions of similar salts of an acid it is practically the same. He confirms in general Ebeling's observation, that the worst conductors are thermoelectrically the most active,. and that some show a maximum thermoelectric force at the concentration of maximum conductivity.   J. W.

Velocity of Ions. By F. KOHLRAUSCH (*Ann. Phys. Chem.*, [2], **50**, 385—408).—In the present paper the author has collected and discussed all the available data bearing on the speed of electrolytic ions, the numerical values being made as far as possible comparable.

First, he gives a table of the Hittorf numbers for the anion of 28 electrolytes at different dilutions. He then shows that the speed of the chlorine ion is the same in solutions of the alkali chlorides at equivalent concentrations from semi-normal downwards, and that the speeds of the two ions of these and similar salts are additive in dilute solutions. As a first approximation, he considers that the increase of the molecular conductivity for the same amount of dilution of different salts is the same.

The following table of the molecular conductivity at infinite dilution and 18°, and the corresponding speeds of the ions is given.   U and V denote the velocities of the kation and anion respectively in centimetres per second; u and v the velocities referred to mercury units; λ the conductivity at infinite dilution.

	λ_∞: 10^{-7}.	u. 10^{-7}.	v. 10^{-7}.	U. 10^{-5}.	V. 10^{-5}.
KCl...............	123	60	63	66	69
NaCl..............	103	41	62	45	69
LiCl..............	95	33	62	36	69
NH$_4$Cl.............	122	60	62	66	68
HCl...............	353	290	63	320	70
KI................	123	60	63	66	69
KNO$_3$.............	118	60	58	66	64
NaNO$_3$............	98	40	58	44	64
AgNO$_3$............	109	52	57	57	63
HNO$_3$.............	350	(290)	(60)	(320)	(65)
KClO$_4$.............	115	(61)	(54)	(67)	(60)
KC$_2$H$_3$O$_2$	94	63	31	69	34
NaC$_2$H$_3$O$_2$...	73	41	32	45	35
KOH...............	2-2	58	165	64	181
NaOH	201	36	165	40	181
AgClO$_3$...	103	51	52	57	57
AgClO$_4$............	106	52	54	57	60
AgC$_2$H$_3$O$_2$...........	83	53	30	58	34
AgC$_9$H$_{11}$SO$_3$.........	73	52	21	57	23

J. W.

Electrical Conductivity of Cupric Chloride Solutions. Γ
R. J. HOLLAND (*Ann. Phys. Chem.*, [2], **50**, 349—360).—Solutions
cupric chloride show a regularly diminishing rate of increase of the
conductivity as the temperature rises, and then varies with the con-
centration, the maximum conductivity being obtained with a solution
containing about 18 per cent. of anhydrous salt. The temperature
coefficient varies with the concentration, and reaches a maximum at
about 40°.   J. W.

**Change of Conductivity of a Solution by the Addition of a
Non-electrolyte.** By R. J. HOLLAND (*Ann. Phys. Chem.*, [2], **50**,
261—292; compare Abstr., 1892, 1382).—The author gives the
following account of his general results.

The electrical conductivity of a solution of an electrolyte in
methylic alcohol diminishes on the addition of a non-conductor, the
diminution varying with the nature of the non-electrolyte and with
the degree of dilution. The four non-electrolytes benzene, toluene,
xylene, and oil of turpentine diminish the conductivity in the order
given. The diminution varies for each volume per cent. of non-
electrolyte added from 1·7 to 2 per cent. of the conductivity of the
corresponding normal solution for 0·01-normal solutions; 1·6—1·75
per cent. for 0·001-normal, and 1·4—1·6 per cent. for 0·0005-normal.

The temperature coefficients of alcoholic solutions increase with
increasing dilution; are only half as great as in the case of aqueous
solutions; and are very little affected by the addition of a non-con-
ductor.

The conductivity of methylic alcohol solutions up to a concentra-
tion of 20 per cent. of non-electrolyte is very exactly represented by
Arrhenius' formula (Abstr., 1892, 1038). No connection between
electrical conductivity and fluid friction was evident.   J. W.

Heat of Dissociation in Electrochemical Theory. By H.
EBERT (*Ann. Phys. Chem.*, [2], **50**, 255—260).—The molecular heat
of dissociation of the hydrogen molecule into atoms, as calculated by
E. Wiedemann, is about $1·1 \times 10^{13}$ ergs; the same magnitude for
iodine, calculated by Boltzmann from Meier and Crafft's data, is
$1·2 \times 10^{12}$ ergs. A calculation on the assumption that the valencies
holding two atoms together are electrical leads to a value for the heat
of dissociation equal to $4·3 \times 10^{12}$ ergs. The author, therefore, con-
cludes that chemical affinity is essentially of an electrical nature.
                                                              J. W.

The Hydrogenation of Closed Chains. BY F. STOHMANN and
H. LANGBEIN (*J. pr. Chem.*, [2], **48**, 447—453; compare Abstr., 1891,
376, 1146).—The following values are given (table, p. 81).

Inasmuch as these values are known for benzene and hexane,
there is now a complete series of values for the hydrogenation of
benzene. A comparison of them shows that the attachment of each
pair of hydrogen atoms to the benzene molecule is not accompanied
by the same thermal change. It must, therefore, be concluded that
there are not three double bonds of equal value in the benzene ring.
The bonds in benzene itself require a greater energy for their opening

| | Heat of combustion of 1 gram molecule. | | Heat of formation from elements. |
	Constant pressure.	Constant volume.	
Dihydrobenzene	848 ·0 Cal.	846 ·8 Cal.	− 8 ·0 Cal.
Tetrahydrobenzene	892 ·0 ,,	890 ·5 ,,	+ 17 ·0 ,,
Hexahydrobenzene....	933 ·2 ,,	931 ·5 ,,	+ 44 ·8 ,,

up than those in any of the hydrogenated benzenes. The bonds in di- and tetra-hydrobenzene require less energy than those of either benzene or hexahydrobenzene, whilst those of the last-named compound require less than those of benzene. A. G. B.

State of Matter near the Critical Point. By B. GALITZINE (*Ann. Phys. Chem.*, [2], **50**, 521—544).—The author arrives at the following conclusions from his observations :—

The temperature of the actual appearance of the meniscus on cooling must lie considerably lower than the critical temperature, so that the optical method as usually carried out by observations of clouding in the tube must lead to erroneous values for the critical point.

If the cooling is conducted very slowly and regularly, there is no clouding.

The temperature at which the meniscus really appears, and the temperature at which the last traces of inhomogeneity vanish, must be regarded as independent of the quantity of substance in the tube.

The density ρ of a liquid in contact with its saturated vapour, and the density δ of this vapour, vary with the time at the same constant temperature, and also if they are heated several times beyond the critical point, ρ decreasing, and δ increasing. These two magnitudes, therefore, are not functions of the temperature alone.

At temperatures considerably higher than the critical point, a substance can have two different densities at almost the same pressure, the difference amounting to as much as 25 per cent.

J. W.

Weight of a Litre of Normal Air : Densities of Gases. By A. LEDUC (*Compt. rend.*, **117**, 1072—1074).—The proportion by weight of oxygen in the air at Sorbonne was found to vary from 23·14 to 23·20 per cent., and since this variation would make a difference of 0·1 milligram in the weight of a litre of air, it is useless to attempt to reach a higher degree of accuracy in such determinations unless the composition of the air is determined at the same time.

The weight of a litre of average air at Paris at 0° and 760 mm. was found to be 1·29315 gram.

The author defines as *normal air* air collected on a plain in calm weather at some distance from a town, and containing a little more than 23·2 per cent. of oxygen by weight, or almost exactly 21·0 per cent. by volume. A litre of such air weighs 1·2932 grams at 0° and 760, and its mass is 1·2758 grams under 1 atmosphere c.g.s.

In accurate estimations of densities of gases it seems preferable to take nitrogen as the standard, since this gas is easily obtained in a state of purity, and its density is so near that of air that the presence of a small quantity of the latter in the apparatus introduces no appreciable error. The weight of a litre of nitrogen at Paris under normal conditions is 1·2570 grams, and its mass under a pressure of 1 atmosphere c.g.s. is 1·24006 grams, or better, 1·24 grams.

<div align="right">C. H. B.</div>

Critical Pressures in Homologous Series of Carbon Compounds. By E. MATHIAS (*Compt. rend.*, **117**, 1082—1085).—In the homologous series of the primary alcohols, the alkyl chlorides, the alkyl salts of formic, acetic, and propionic acids, the simple and mixed ethers, and the alkyl derivatives of ammonia, the critical pressures π, like the critical densities, are a continuous function of the total weight of the molecule, and, except in the case of the ammonia derivatives, it is possible to pass from one curve to the other by a simple linear substitution of the form $\pi' = \alpha\pi + \beta$; α and β being numerical constants which separately may be *nil*. Within the limits of the experimental errors, the curves of the critical pressures can be assimilated to arcs of equilateral hyperbolas, with asymptotes parallel with the axes of the coordinates, and can, therefore, be represented by the equation $(\pi + a)(n + b) = c$. In the case of the alcohols, and, therefore, in all the monosubstitution derivatives, $b = 3$.

By the method of substitution it is found that the critical pressure of hydrogen is 72·66 atmos., a value which is much higher than that obtained directly by Wroblewski, and which explains the difficulty of obtaining liquid hydrogen in a static condition.

The critical pressures of the alkyl salts derived from the primary alcohols are represented by the formula

$$\pi = \tfrac{1}{2}n' + 7\cdot5 + \frac{600}{(n + 3)(n' + 4)},$$

where n' is the number of carbon atoms in the acid.

The critical densities Δ and the critical pressures π in a given homologous series being continuous functions of the molecular weights, it follows that in each series there is a relation between Δ and π which is independent of the particular compound considered.

<div align="right">C. H. B.</div>

Dissociation of Water. By J. J. A. WIJS (*Zeit. physikal. Chem.*, **12**, 514—523).—In a former paper (Abstr., 1893, ii, 364), the extent to which pure water may be regarded as dissociated electrolytically was calculated from the rate of hydrolysis of methylic acetate by water. The number then obtained was considered as being too low, owing to the fact that the acetic acid liberated in the reaction retards the hydrolysis during the first period, by the influence of its dissociated hydrogen ions on the hydroxyl ions of the water. In order to calculate and allow for this influence, fresh determinations of the rate of hydrolysis of methylic acetate by water have been made, the acetic acid liberated being determined by measuring the conductivity of the solution. From these results the concentration of the hydroxyl ions in water is calculated as $0\cdot14 \times 10^{-6}$, but the author is somewhat

doubtful of the purity of the water used, and proposes to repeat the experiment under circumstances that will ensure greater accuracy.

H. C.

Action of Salts on Acids. By R. W. WOOD (*Amer. Chem. J.*, **15**, 663—670).—Duggan's work on "absolute neutrality" (Abstr., 1886, 765) cannot be considered conclusive, as the diastase used as an indicator was not sensitive enough. His view that the amylolytic function of that ferment is due to the presence of small traces of acid or alkali is not in accordance with his experimental results. It is more probable that the inhibition is due to free ions, of hydrogen in the case of acids, and of hydroxyl in the case of alkalis, "absolute neutrality" occurring only when these ions are formed at equal rates. The salts of "weak" acids in solution may be regarded as partly hydrolysed into the acids and bases; and as the latter split up more readily than the former, there is a tendency for normal salts to appear alkaline towards diastase.

The author prepares diastase directly from pale barley-malt by precipitating the cold aqueous extract with alcohol, and drying the washed precipitate in a vacuum over sulphuric acid. The ferment thus obtained is both powerful and sensitive; it is capable of hydrolysing 70 times its weight of starch, and the rate of hydrolysis is distinctly lowered by the addition of 1 part per million of sodium hydroxide (phenolphthaleïn is sensitive only to 8 parts per million).

The experiments were made on a uniform plan. The emulsion of starch (2 grams in 80 c.c. of water) was heated to 55° in a chamber surrounded by acetone vapour, the diastase (0·01 gram) added, and the mixture heated for 30 minutes. Aqueous soda (2 c.c. of 10 per cent.) was then added to inhibit the action of the diastase, and the reducing sugar formed estimated with alkaline copper tartrate.

The inhibitory effect of acids is less powerful than that of alkalis. In every case the initial action is to increase the activity; this is probably due to the presence of a trace of impurity in the starch. The action of the first five normal acids of the fatty series is much affected by temperature, the inhibitory power of the acids increasing faster than the hydrolytic power of the diastase.

Neutral salts of "weak" acids have a slight inhibitory action, as stated above, but those of "strong" acids are without action; in general, the "weaker" the acid the less the effect. The addition of free acid to normal salts first increases the inhibitory effect and then decreases it; but the variation is less marked than in the absence of the salt. At the maximum, the amount of acid may be varied between considerable limits without affecting the rate of hydrolysis. This is probably due to a want of sensitiveness even of the purer diastase; Duggan's results, therefore (*loc. cit.*), may readily be accounted for.

JN. W.

Freezing Point of Dilute Solutions. By H. C. JONES (*Zeit. physikal. Chem.*, **12**, 623—656).—The author has determined the freezing points of the solutions of the following electrolytes between the limits of about 1/10 normal and 1/1000 normal:—Hydrochloric acid, sulphuric acid, nitric acid, phosphoric acid, potassium hydroxide, sodium hydroxide, ammonia, potassium carb-

onate, and sodium carbonate. In general the degree of dissociation calculated from the depression of the freezing point agrees fairly well with that calculated from the electric conductivity, being somewhat less in the case of the acids and bases, and affected by hydrolysis in the case of the carbonates.

The following organic compounds (practically non-electrolytes) were also investigated :—Cane sugar, glucose, carbamide, phenol, ethylic alcohol, propylic alcohol. The depression constant obtained for the most dilute solutions of these substances is much greater than the calculated constant for water. With increasing concentration, the molecular depression sinks to a minimum, and then either remains constant, or again increases, as in the case of the two carbohydrates. With phenol, the minimum was apparently not reached.

For the feeble conductors acetic acid and succinic acid, there is an approximate agreement between the values of the dissociation ratio calculated from the freezing point depression and from the electrical conductivity.

The depression constants obtained for water from solutions of carbamide, ethylic alcohol, and propylic alcohol were 1·888, 1·876, and 1·878 respectively, the value calculated from the latent heat of fusion (79·7), by means of Van't Hoff's formula, being 1·87.   J. W.

Rate of Crystallisation of Supercooled Liquids. By B. MOORE (*Zeit. physikal. Chem.*, **12**, 545—554).—A ∪-tube, open at both ends, was filled with a liquid (for example, acetic acid), and kept at a constant temperature below the freezing point of the latter. Crystallisation of the overcooled liquid was then induced in one limb, and the time taken for the boundary between the solid and liquid to pass downwards from one mark to another on that limb was noted. This time was found to be independent of the width of the tube, and approximately inversely proportional to the degree of overcooling. Experiments were made with phenol containing various proportions of water, in order to ascertain if the rate of crystallisation remained the same for the same degree of overcooling of the different mixtures. This was found not to be the case, the velocity in the mixture increasing at a much smaller rate with the degree of overcooling than when phenol alone was used. Cresol mixed with phenol greatly diminished the rate of crystallisation.   J. W.

Solubility of Mixed Crystals. By A. FOCK (*Zeit. physikal. Chem.*, **12**, 657—662).—The isomorphous double salts $2KCl,CuCl_2,2H_2O$ and $2NH_4Cl,CuCl_2,2H_2O$ were mixed in various proportions, dissolved in water, and the solutions allowed to crystallise by spontaneous evaporation at 17°. As soon as a quantity of mixed crystals sufficient for analysis had separated, they were removed and analysed along with a sample of the solution taken at the same time. The solutions always contained a larger proportion of the salt $2KCl,CuCl_2,2H_2O$ than the mixed crystals, and as evaporation proceeded, proportionately more and more ammonium salt was removed from the solution. The series of mixtures, however, is not continuous, crystals containing 27·77 and 54·87 molecules of $2KCl,CuCl_2,2H_2O$ per cent. respectively forming the

limits at the temperature observed. The replacement of ammonium by potassium in the solution appears to cease when these limiting crystals exist together in contact with the solution, the composition of the solution remaining constant until all the crystals of 27·77 per cent. have been removed, or transformed into those of 54·87 per cent.

When solutions of ammonium sulphate and potassium sulphate were allowed to crystallise together, it was found that the molecular percentage of ammonium sulphate in the mixed crystals was very nearly proportional to the concentration of the solution with respect to ammonium sulphate.   J. W.

Isomorphism. Part VIII. By J. W. RETGERS (*Zeit. physikal. Chem.*, **12**, 583—622; compare Abstr., 1891, 146, and 1151; Abstr., 1892, 1048; Abstr., 1893, ii, 161).—Schröder van der Kolk (Abstr., 1893, ii, 280) suggested that the ferric chloride contained in Scheele's ruby-coloured ammonium chloride crystals might be in the form of an isomorphous admixture of the regular hydrate of ferric chloride described by him. The author rejects this suggestion on the ground that the regular hydrate of ferric chloride is colourless, and could not produce the intense colour of the mixed crystals. He is of opinion that isomorphism in this case is altogether excluded, and that the most satisfactory explanation is that the ferric chloride is merely an enclosed hydrate, probably $Fe_2Cl_6,7H_2O$. The regular crystals he considers to be most probably an unstable form of a hydrate with much more water than the yellow hydrate, $Fe_2Cl_6,12H_2O$.

When sulphur and selenium crystallise together from their solution in methylenic iodide, the sulphur crystals are coloured yellowish-brown by admixture of selenium. No such mixed crystals are formed when sulphur and tellurium are crystallised simultaneously from warm methylenic iodide. The sulphur crystals in this case are pale yellow, and crystallise out quite independently of the opaque, metallic tellurium which separates beside them. The author consideis that this shows that whilst sulphur and selenium are isodimorphous, sulphur and tellurium are not.

From an extensive series of experiments on the crystallisation of salts from aqueous solutions strongly coloured by organic dyes, the author finds that in almost all cases colourless crystals separate. The exceptions are strontium nitrate, which is coloured by vegetable dyes, as observed by Sénarmont; potassium sulphate, which is coloured by Bismarck-brown; potassium nitrate, which is coloured by nigrosin; ammonium nitrate, which is coloured by indulin; and barium chloride, which is coloured by "Wasserblau." Sénarmont's speculation that salts with much water of crystallisation would show the property of absorbing colouring matters was not confirmed, most of the above-mentioned salts being anhydrous, and no coloration taking place with such strongly hydrated salts as Glauber's salt, alum, sodium thiosulphate, and sodium phosphate.

                                                                J. W.

Endothermic Reactions effected by Mechanical Force. By M. C. LEA (*Amer. J. Sci.*, [3], **46**, 241—244).—In a former paper

(Abstr., 1893, ii, 69), the author showed that silver haloïds may be decomposed by the application of a high pressure, and he has been thus led to examine whether the same agent, mechanical force, would not be capable of bringing about analogous chemical changes in other compounds. Pressure was applied as before by means of a combination of screw and lever, the calculated maximum pressure obtainable without allowing for loss by friction being over a million pounds per square inch. The material was wrapped in either platinum or silver, usually platinum, foil. There was no action in any case on the metal, which preserved its full brightness in the parts in contact with the material, so that the effects observed were due to pressure only.

Silver sulphite in platinum foil was moderately darkened by two days pressure. Silver salicylate was rendered very dark by two days pressure. Silver carbonate was moderately darkened by a somewhat longer pressure. Silver tartrate and silver oxide were not affected.

Ferric oxide, recently precipitated and dried, was unaffected by pressure, no ferrous oxide being formed.

Potassium Platinobromide.—Where the pressure was greatest the brilliant red colour of this substance was blackened, not superficially only, but all through. Ammonium platinobromide showed moderate but well marked darkening.

Potassium Chlorate.—When this substance was subjected to pressure by itself, no effect whatever was produced, and not a trace of chloride was formed. But when it was mixed with silver nitrate, both in fine powder, and subjected to pressure, there was an evident formation of silver chloride. The material was no longer completely soluble in water, but left an abundance of white flakes which darkened when exposed to light.

Mercuric oxide darkens slightly but very distinctly, and this change seems to be accompanied by a slight loss of weight, requiring, however, very careful weighing to detect it. The darkened part, as well as the rest, dissolves without difficulty in acetic acid, and consisted, therefore, probably of traces of mercurous oxide and not of metallic mercury. Mercurous chloride and mercuric chloride remained unchanged. Mercuric iodide darkened considerably. and at points where the pressure was greatest, it became absolutely black. It did not appear, however, that any iodine was set free ; none could be extracted with alcohol. With mercuric oxychloride, $2HgO,HgCl_2$, heavy pressure caused much darkening.

Sodium thiosulphate compresses to a hard, translucent cake, but does not decompose.

Although in all these instances the darkening is well marked, the actual proportion of material affected is small, so that in many cases it is difficult to apply tests to decide as to the precise nature of the substances formed. In some cases, however, this can be done, and the author concludes that many of the salts of easily reducible metals, especially of silver, mercury, and platinum, undergo reduction by pressure. Such reactions are endothermic, and it therefore follows that mechanical force can bring about reactions which require expenditure of energy, which energy is supplied by mechanical force

in the same way that light, heat, and electricity supply energy in the endothermic changes which they bring about. H. C.

Note by Abstractor.—Formation of allotropic modifications, at any rate in the case of the mercuric compounds, appears possible.
H. C.

The Diamond as the Standard for the Determination of Atomic Weights. By G. HINRICHS (*Compt. rend.*, **117**, 1075—1078). —The author proposes that the diamond should be adopted as the standard matter for the determination of atomic weights. It is solid, compact, non-absorptive, and sufficiently hard to resist the mechanical effects of the necessary manipulations, and its resistance to the action of energetic chemical reagents makes the removal of impurities comparatively easy. Moreover, its purity is unquestionable, and it is not liable to contain mechanical inclusions. Oxygen has almost invariably to be determined by difference, whilst hydrogen is probably the worst standard that could be selected, owing to its low atomic weight, the difficulties of manipulation, and the difficulty of obtaining it pure.

If $C = 12$, it follows from the determinations of Dumas, Erdmann, Marchand, and Roscoe that $O = 16$, and from the determination of Erdmann and Marchand, that $Ca = 40$.

The mutual dependence of all the atomic weights can be represented by means of a parabola, with diamond at the vertex and calcium at the focus, the primary elements being placed on the curve at the proper distance from the vertical passing through the zero of the atomic weights. The secondary axis passing through this point will be the locus of the atomic weights determined indirectly. Adopting recognised experimental results, it appears that, with very small errors, $P = 31$, $Fe = 56$, $Zn = 65·5$, $Cd = 112$, $Hg = 200$, $Pb = 207$, and $H = 1·0$, $Mg = 24$, $S = 32$, $Be = 9$, $Cu = 63·5$, and $F = 19$. For the proper determination of the atomic weights of the halogens, a revision of the atomic weight of silver is necessary, and this element might then serve as a secondary standard.
C. H. B.

Beckmann's Method for determining Molecular Weights. By G. BARONI (*Gazzetta*, **23**, ii, 249—291; compare Abstr., 1893, ii, 511).—The small variations in the barometric height which often occur during the determination of molecular weights by Beckmann's method have a considerable influence on the accuracy of the result; they are, therefore, not negligible, as is usually supposed. The error introduced by variations in the atmospheric pressure during the determination may amount to one-half the molecular weight of the substance. The author has determined the molecular weight of sodium bromide, strontium and mercuric chlorides, potassium and silver nitrates, potassium sulphate, chromate, and dichromate, iodic, succinic, oxalic, tartaric, and citric acids, mannitol, and cane sugar in aqueous solution, and of phenol and resorcinol, using benzene as the solvent. The curves plotted with the concentrations as abscissæ and the molecular weights as ordinates rise, in the majority of cases, in accordance with the requirements of the dissociation hypothesis.

The curves obtained for potassium chromate, bromide, and chloride, and for citric acid, first rise and then fall; in the cases of barium, sodium, and strontium chlorides, sodium bromide, and tartaric acid, the curves fall throughout the whole length examined. The cause of this behaviour is unknown.   W. J. P.

Graphochemistry of Oxides and their Combinations. By E. NICKEL (*Zeit. physikal. Chem.*, **12**, 663—669).—The author has applied his graphochemical method (compare Abstr., 1892, 1158) to the tabulation of the oxides with respect to their composition, properties, and combinations with each other. To obtain a table for their composition, he makes use of the following considerations. If E is the symbol of an element, each oxide may be expressed as EO_n, and if p be the atomic weight of the element and x the percentage of oxygen in the oxide, then $p/16n = (100 - x)/x$. The table is constructed by taking the values of p and n (or $16n$) as ordinates and abscissæ respectively, x then appearing as a bundle of rays diverging from the origin. All the oxides of each element are found in a horizontal line, and all the oxides with the same atomic oxygen ratio in the same vertical line. If the elements are gone through in the order of their atomic weights, a curve like Lothar Meyer's spiral is obtained when the typical oxides are considered.   J. W.

Inorganic Chemistry.

Molecular Weight of Hydrogen Peroxide. By G. TAMMANN (*Zeit. physikal. Chem.*, **12**, 431—432).—A redetermination of the molecular weight of hydrogen peroxide by the cryoscopic method gives the molecular formula H_2O_2, in place of H_4O_4 as formerly given by the author (Abstr., 1890, 106), and accords, therefore, with the results of Carrara's determination (Abstr., 1893, ii, 163).

H. C.

Occurrence of Hydrogen Peroxide in the Atmosphere and in Atmospheric Discharges. By E SCHÖNE (*Ber.*, **26**, 3011—3027).—During 1874-75 the author carried out systematic observations of the atmosphere in the neighbourhood of Moscow, and was led to affirm the presence in it of hydrogen peroxide. This conclusion was questioned by L. Ilosvay in 1889, whose arguments may be thus summarised. 1. The reactions with potassium iodide, starch, ferrous sulphate, guaiacum tincture, and malt extract are not characteristic of hydrogen peroxide, and may also be produced by nitrous acid. 2. Characteristic reagents fail to show the presence of hydrogen peroxide in the atmosphere. 3. No chemical process is known by which hydrogen peroxide and ozone are produced in nature. 4. Ozone is not formed during rapid combustion, and hydrogen peroxide only in circumstances which prevent its passing into the atmosphere. 5. The

negative results obtained from certain special experiments designed to show the presence of hydrogen peroxide. The author criticises and refutes these conclusions in detail. 1. Ilosvay's statements about the reagents are partly due to errors of manipulation and partly to lack of precautions in the preparation of the various solutions. 2. Titanic acid, which is stated to be the only characteristic reagent for hydrogen peroxide, is capable of detecting not less than 1 : 90,000, but in only two cases out of 500 has the author found more than 1 : 1,000,000. 3. Apart from electrical discharges, the author suggests that the action of sunlight, air, and moisture on ethereal oils and similar substances would result in the production of ozone and of hydrogen peroxide. 4. The formation of hydrogen peroxide during combustion has been proved by the independent observations of several chemists by more exact methods than Ilosvay's. 5. The results of Ilosvay's crucial experiments are invalid for the following reasons. (a) The air was taken from the streets of Budapest; (b) the volume (171—500 lit.) was far too small; (c) as hydrogen peroxide is unstable in presence of alkalis, the soda employed to absorb it would cause its decomposition during the long continuance (2—5 weeks) of the experiments; (d) the passage of the air through the various purifying solutions (soda and dilute sulphuric acid) would cause the complete absorption of hydrogen peroxide, and consequently account for the various reagents such as thallium paper and azo-benzenenaphthylamine being unaffected. Samples of rain water, tested during the past two years, show that there is no connection between the quantities of hydrogen peroxide and nitrites which they contain.   J. B. T.

Manufacture of Oxygen from Calcium Plumbate. By G. KASSNER (*Chem. Zeit.*, **17**, 1242).—In investigating the dissociation of calcium plumbate, H. Le Chatelier (Abstr., 1893, ii, 524) found that for the evolution of oxygen by heat alone it is necessary to raise temperature about 200° higher than in the case of barium peroxide; on the other hand, at lower temperatures the oxygen is more quickly and completely reabsorbed from air by the plumbate than by the barium oxide. The author now calls attention to the fact that whilst in his earlier communications he mentioned the evolution of oxygen from calcium plumbate by heat alone, he recommended, as more generally useful, several other methods; the following is especially advantageous. Porous calcium plumbate is moistened with steam and subjected to the action of washed furnace gases, preferably, at a temperature below 100°. The carbonic anhydride of the furnace gases is rapidly absorbed, and the material, which retains its porous condition, then consists of a mixture of calcium carbonate and lead peroxide. This is transferred to a retort kept constantly at a red heat, and in this the oxygen is evolved, the evolution being much helped by the introduction of a current of steam. After the evolution of the oxygen, the current of steam is continued, and the temperature raised, when carbonic anhydride is liberated, and may be collected for use. The calcium plumbate is then regenerated by means of a current of air. The author also refers to Peitz's patented

modification, in which it is proposed to decompose the plumbate by means of a current of pure carbonic anhydride at a red heat.

The author claims for his plumbate process, as advantages over the Brin barium oxide process, (*a*) obtaining pure carbonic anhydride as a bye-product; (*b*) the use of low temperatures, and consequent saving in fuel and in wear and tear of retorts. (See also Abstr., 1891, 392.)   L. T. T.

Molecular Weight of Persulphates and Permolybdates. By G. MOELLER (*Zeit. physikal. Chem.*, **12**, 555—563).—The molecular weights of potassium persulphate and of ammonium persulphate were found by the author, from a consideration of the electrical conductivity and the cryoscopic behaviour of their solutions, to be in correspondence with the formulæ $K_2S_2O_8$ and $(NH_4)_2S_2O_8$ (compare Bredig, Abstr., 1893, ii, 572).

The conductivity and freezing point depressions of Péchard's potassium permolybdate and ammonium permolybdate point to these substances having the formulæ $K_2Mo_2O_8$ and $(NH_4)_2Mo_2O_8$ respectively.   J. W.

Action of Nitric Peroxide on Metals and Metallic Oxides. By P. SABATIER and J. B. SENDERENS (*Bull. Soc. Chim.*, [3], **9**, 668—669 ; compare Abstr., 1892, 1390).—Brown tungstic dioxide becomes incandescent in nitric peroxide at 300°, and yields yellow tungstic anhydride mixed with a little blue oxide, W_2O_5.

Sodium is not oxidised by nitric peroxide in the cold, and is but slowly attacked on heating. Reduced nickel ignites at the ordinary temperature, and forms nickelous oxide.   W. T.

A New Sulphide of Carbon. By B. v. LENGYEL (*Ber.*, **26**, 2960—2968).—When pure, dry carbon bisulphide is boiled in a reflux apparatus, the vapour being exposed to an electric arc maintained between two carbon poles for two or three hours, the interior of the apparatus becomes blackened, and a black substance is found suspended in the liquid. If this is filtered off, a cherry-red liquid is obtained, which has a remarkably strong odour, and produces great irritation of the eyes. This liquid is allowed to stand for 6—8 days over metallic copper to remove free sulphur, and is then evaporated by means of a current of dry air. A deep red liquid is thus left which has the composition of a *tricarbon bisulphide*, C_3S_2. It evaporates in the air very slowly, and its vapour has a most vigorous action on the mucous membrane, a very small trace causing violent catarrh. Placed on the skin, it merely produces a black spot. The sp. gr. of the liquid is 1·27389. When heated, it is converted into a hard, black mass of almost the same percentage composition, which is probably a polymeride. When the liquid is rapidly heated to 100—120°, this change takes place with explosive violence, but occurs gradually when it is gently warmed. The same substance is formed when the liquid is preserved for a few weeks, and its formation is in all cases accompanied by the production of a little carbon bisulphide. The liquid can be distilled under diminished pressure at 60—70°, but

a portion of it is always converted into the solid modification. The liquid substance is insoluble in water, in which it sinks, but is readily soluble in alcohol, ether, chloroform, benzene, and carbon bisulphide. From a concentrated solution in the solvent last mentioned, the solid modification is deposited, but a dilute solution is more stable. It burns with a luminous, smoky flame, carbonic and sulphurous anhydrides being formed. Aqueous potash and soda give almost black solutions, in which acids produce black precipitates, whilst alcoholic potash acts vigorously and yields a deep brown solution. A drop of concentrated sulphuric acid causes violent hissing, and the whole mass is converted into the solid modification. Concentrated nitric acid causes ignition, whilst a more dilute acid dissolves the liquid, neither carbonic anhydride nor sulphuric acid being formed.

The analyses of the liquid show rather less carbon, those of the solid rather more, than that required by the formula C_3S_2. A determination of the molecular weight from the freezing point of the solution in benzene gave numbers which agree well with the formula.

The solid modification is hard, has a fine, granular fracture, and is insoluble in water and all ordinary solvents. Aqueous potash dissolves it completely, and it appears to be precipitated unaltered on the addition of an acid. When heated, it decomposes, with formation of sulphur, which sublimes, and a gas which contains sulphur, but is not carbon bisulphide, and is being further investigated.

When bromine is added to a solution of the liquid tricarbon disulphide in chloroform, heat is evolved, and a yellow precipitate produced; this has the composition $C_3S_2Br_6$, has an aromatic odour, and is insoluble, or only very slightly soluble, in all solvents. Under similar conditions, a yellow precipitate is produced with chlorine, but not with iodine.

The author is investigating the structure of this bromide.

A. H.

Preparation of Metallic Lithium. By GUNTZ (*Compt. rend.*, **117**, 732—733).—In the preparation of lithium, the yield is higher the lower the temperature at which electrolysis takes place. Lithium chloride melts at 600°, a mixture of equal weights of lithium and potassium chlorides melts at about 450°, and a mixture of the two chlorides in molecular proportion at about 380°; a mixture of 2 mols. of potassium chloride with 1 mol. of lithium chloride melts at about 550°, and potassium chloride alone at 740°.

The best mixture for electrolysis contains equal weights of the two chlorides, for then the melting point of the saline mixture falls as decomposition proceeds. The negative electrode should be a rod of carbon about 8 mm. in diameter, and the positive electrode a rod of iron 3 to 4 mm. in diameter, surrounded by a glass tube about 20 mm. in diameter. A current of 20 volts and 90 ampères is necessary, and the metal obtained contains from 1 to 2 per cent. of potassium.

It would seem that when electrolysis takes place at a red heat, the lithium at the negative electrode combines with the lithium chloride to form a subchloride, Li_2Cl, which has a higher resistance than the original chloride, and thus reduces the intensity of the current. The

subchloride diffuses through the liquid and combines with chlorine at the positive electrode. At 500°, or below, it would seem that this formation of subchloride does not take place.   C. H. B.

Calcium Oxyiodide. By TASSILLY (*Bull. Soc. Chim.*, [3], **9**, 629—630).—Calcium oxyiodide, $CaI_2,3CaO + 16H_2O$, has been obtained in needles, sometimes 2 cm. long, by heating quicklime with a concentrated solution of calcium iodide in a sealed tube at 150° for six hours. It is also formed by the addition of quicklime in small portions to a boiling concentrated solution of calcium iodide. Long needles are obtained on cooling this solution, which cannot be freed from adhering lime.   W. T.

Double Salts of Potassium and Magnesium Sulphate: Schönite and Potassium Astrachanite. By J. K. VAN DER HEIDE (*Zeit. physikal. Chem.*, 12, 416—430).—The author has already recorded the formation of potassium astrachanite, $MgSO_4,K_2SO_4,4H_2O$, from a solution of schönite, $MgSO_4,K_2SO_4,6H_2O$ (Abstr., 1893, ii, 276), and in order to obtain further data respecting the conditions under which it is produced, has now examined the behaviour of the sulphates of potassium and magnesium towards one another in solution at all possible temperatures. The following are the principal facts resulting from this investigation.

1. Temperature, $-4·5°$. Formation from ice and the two sulphates of the saturated solution of the latter.

2. Temperature, $-3°$. Formation of schönite from the two sulphates

3. Temperature, $47·2°$. $MgSO_4,7H_2O$, changes in the presence of schönite into $MgSO_4,6H_2O$.

4. Temperature, $72°$. Potassium astrachanite is formed from schönite in the presence of $MgSO_4,6H_2O$.

5. Temperature, $92°$. Potassium astrachanite is formed from schönite in the presence of K_2SO_4.

6a. Temperature, $102°$. Boiling point of the saturated solution of potassium astrachanite and sulphate.

6b. Temperature, $103°$. Boiling point of the saturated solution of potassium astrachanite and $MgSO_4,6H_2O$.

7. Temperature, $106°$. Formation of kieserite in the presence of potassium astrachanite.   H. C.

Modifications of Silver. By H. LÜDTKE (*Ann. Phys. Chem.*, [2], **50**, 678—695).—The silver of deposited silver mirrors has properties different from those of ordinary silver, and the author has investigated these electrically with the following results.

Lehmann's assumption that a thin layer of sodium silicate on all glass surfaces has something to do electrolytically with the deposition of silver, must be incorrect, for silver mirrors may be deposited on mica, porcelain, quartz, Iceland spar, platinum, &c.

The electrical resistance of several sorts of silver mirrors decreases considerably as time elapses. There is no such decrease in the case of mirrors reduced by milk sugar or by Martin's method.

The allotropic mirror silver may easily be converted into ordinary silver by heat, light, chemical reagents, &c.

The mirror silver and other allotropic preparations show an initial difference of potential of about 0·1 volt against ordinary silver in dilute acids, the allotropic modification being the positive pole. The difference is smaller in silver nitrate solution, and the ordinary silver is then the positive pole.

All the properties of mirror silver indicate that in its original modification it is identical with solid colloidal silver.

The black silver sponge obtained by reducing silver nitrate solution with zinc passes into a grey modification on contact with acids. This transformation is accompanied by an increase in the electric conductivity. J. W.

Method of Formation of Silver Nitride. By A. ANGELI (*Gazzetta*, **23**, ii, 292—294).—On adding a saturated hydrazine sulphate solution to a cold saturated solution of silver nitrite, the liquid immediately becomes turbid, and silver nitride separates in white needles. The reaction probably proceeds in accordance with the following equations.

$$NH_2 \cdot NH_2 + HNO_2 = NH_2 \cdot N:N \cdot OH + H_2O.$$
$$NH_2 \cdot N:N \cdot OH = N_3H + H_2O.$$
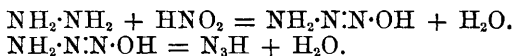
This simple method of preparing the salt forms a very striking lecture experiment, and may be very rapidly performed.
W. J. P.

Preparation of Cuprous Oxide. By E. J. RUSSELL (*Chem. News*, **68**, 308).—A fairly concentrated solution of copper sulphate along with excess of sodium chloride is thoroughly reduced by treatment with gaseous sulphurous anhydride, the excess of the latter is then expelled by heating, and solid sodium carbonate is added to the hot solution ; bright red cuprous oxide is precipitated and is readily washed by decantation. D. A. L.

Stability of Dilute Solutions of Mercuric Chloride. By L. VIGNON (*Compt. rend.*, **117**, 793—795).—Aqueous solutions containing 0·1 per cent. of mercuric chloride gradually deposit a white precipitate if exposed to the air, but remain practically unchanged for many days in well closed vessels. In presence of magenta or indigo-carmine the quantity of precipitate formed in a given time is reduced, and in this respect indigo-carmine is a better preservative than magenta. In presence of 0·1 per cent. of hydrochloric acid of 22°, or of 1 per cent. of sodium, ammonium, or potassium chloride, the solution remains practically unchanged for a much longer time.
C. H. B.

Stability of Mercuric Chloride Solutions. By TANRET (*Compt. rend.*, **117**, 1081—1082).—The formation of a white precipitate in dilute solutions of mercuric chloride (preceding abstract) is due to the presence of ammonia in the atmosphere, and does not take place with pure air even when large quantities of the latter are passed through the liquid. C. H. B.

Action of Mercurous Chloride on Silver Chloride in presence of Ammonia. By U. ANTONY and G. TURI (*Gazzetta*, **23**, ii, 231— 237).—Pesci (Abstr., 1892, 685) has shown that the black precipitate obtained by treating mercurous chloride with ammonia contains metallic mercury; this observation explains the well-known fact that, on adding ammonia to the white precipitate obtained with hydrochloric acid in a mixed solution of silver and mercurous salts, silver is retained in the black precipitate. If the precipitate remains long in contact with ammonia, the reaction represented by the following equation may occur:—

$$4HgCl + 4AgCl + 8NH_3 = 2(NHg_2Cl,NH_4Cl) + 4Ag + 4NH_4Cl.$$

On repeatedly washing the mixture of silver chloride and mercurous chloride with ammonia solution on a filter, a residue was ultimately obtained which contained 1·16 per cent. of silver, instead of 30 per cent. as indicated by the above equation. When, however, the mixed chlorides precipitated from a solution containing excess of silver salt were digested with ammonia for some time, the resulting precipitate was found to contain the quantity of silver indicated by the equation. During a qualitative analysis, therefore, if silver is not found in the filtrate from this black precipitate, the latter should be examined for the metal. W. J. P.

Sublimation of Red and Yellow Mercuric Iodides. By BERTHELOT (*Compt. rend.*, **117**, 827—828).—The author confirms Frankenheim's statement that when a mixture of red and yellow mercuric iodides is carefully heated on a glass plate and allowed to condense on another plate held at a short distance above it, the sublimate is a mixture of the red and yellow iodides. The result, however, cannot be regarded as proof of the existence of the red iodide in the state of vapour. There is little doubt that solid particles of the red iodide are mechanically projected from the lower plate to the upper, and bring about the immediate conversion of the yellow iodide that condenses in contact with them. C. H. B.

Action of Water on Glass. By F. KOHLRAUSCH (*Ber.*, **26**, 2998—3003).—Analyses have been made of the substances extracted by water at ordinary temperatures from finely powdered glass of various kinds. A comparison of the soluble portion with the original glass shows that, in the former, the relative quantity of alkali increases and that of the silica diminishes; in one case, the solution contained three times as much alkali and half as much silica as the original glass, which was rich in alkali. With Bohemian potash glass (rich in silica), the discrepancy was less. Both of these glasses are largely employed in the manufacture of chemical apparatus. At present, it is impossible to decide whether the solution of the alkali precedes and causes that of the silica, but the author's experiments show that practically they dissolve simultaneously.

A sample of Jena "apparatus" glass and two of a glass free from alkali were examined in a similar manner, and, after two months' treatment with water, the solutions contained 72, 85, and 57 milli-

grams per litre respectively. A flask of the Jena glass, after two days at ordinary temperatures, lost 0·005 milligram, after 200 days 0·066 milligram, after 24 hours at 94°, 0·8 milligram per sq. dm. Experiments were also conducted to show the relative insulating power of different sorts of glass under varying conditions of atmospheric moisture; glass of poor quality conducts after exposure for a few seconds in presence of 40—50 per cent. of moisture, whilst the glass free from alkali insulates well in presence of 80 per cent. The composition of the alkali-free glass, in equivalents per cent., is as follows:—BaO = 12, ZnO = 3·7—4·6, Al_2O_3 = 3·3—3·7, B_2O_3 = 13—15, SiO_2 = 65—68.   J. B. T.

Nitro-metals. By P. SABATIER and J. B. SENDERENS (*Bull. Soc. Chim.*, [3], **9**, 669—674; compare Abstr., 1892, 1390; 1893, ii, 374). —*Nitro-cobalt.*—This substance is best prepared from cobalt reduced at a low temperature. Nitrogen peroxide, suitably diluted with nitrogen, is passed over the reduced metal in the reduction tube, when black nitro-cobalt, Co_2NO_2, is formed. Water acts on nitro-cobalt very vigorously, but gives less nitric oxide than with nitro-copper. A solution of cobalt nitrate containing very little nitrite is produced, with, sometimes, a precipitate of bluish-green, insoluble basic nitrite mixed with cobalt. Heated in a current of nitrogen, nitrous fumes are first evolved, and then decomposition takes place with almost explosive violence, a residue of metallic cobalt and oxide being formed. Nitro-cobalt explodes when mixed with combustible matter.

Nitro-nickel.—This compound resembles the cobalt compound in method of formation and properties; it has always been obtained mixed with oxide. It appears to give no special reaction with carbonic oxide.

Nitro iron.—This substance is much more difficult to prepare. Some nitric peroxide is first absorbed, and then deflagration takes place, even in a much diluted atmosphere of nitric peroxide.

W. T.

Chromium Sulphates and Double Sulphates. By T. KLOBB (*Bull. Soc. Chim.*, [3], **9**, 663—668).—The double sulphate, $Cr_2(SO_4)_3,3(NH_4)_2SO_4$, has been prepared by adding chromic oxide to a large excess of ammonium sulphate kept in a state of quiet fusion. In this case, a clear, green, crystalline powder is obtained, whilst if violet ammonium chromium alum is substituted for the oxide, a pulverulent powder is obtained not so readily washed. It forms needles, 0·05 mm. long, and short spindles. The crystals are but slightly attacked by boiling water, not acted on by a concentrated solution of ammonium sulphate, and completely decomposed by boiling potash. Boiling concentrated sulphuric acid gives Traube's red sulphate. The salt is not decomposed by heating at 350° on a lead bath, but takes a transient violet colour. By calcination, it yields a very adherent, light oxide.

The double sulphate, $Cr_2(SO_4)_3,(NH_4)_2SO_4$, is formed if the preceding preparation be heated so far as to volatilise most of the ammonium sulphate. It forms tabular, hexagonal crystals, which are more stable

than the needles described above, as they are not attacked by boiling water or concentrated hydrochloric acid; boiling potash (sp. gr. 1·3) acts on them but very slowly. Heat and concentrated sulphuric acid have the same action as on the needles.

These double sulphates correspond with the ferric ammonium sulphates obtained by Lachaud and Lepierre. They may be viewed as derivatives of Recoura's chromosulphuric acid, $H_2Cr_2(SO_4)_4$, and chromotrisulphuric acid, $H_2Cr_2(SO_4)_6$ (Abstr., 1893, ii, 470).

Attempts to prepare the corresponding potassium and sodium salts failed, as the chromosulphates could not be obtained free from ammonia; potassium chromotrisulphate is obtained by fusing potassium chromium alum with excess of ammonium sulphate and potassium sulphate.

The red sulphate of chromium, referred to above, prepared in three different ways, has the formula $Cr_2(SO_4)_3$, and is, therefore, a normal salt. It is a powder, rose-coloured in daylight, but appears green by gas-light. W. T.

Complex Acids derived from Molybdic acid and Titanic and Zirconic acids. By E. Péchard (*Compt. rend.*, 117, 788—790).— When hydrofluosilicic acid is added to a warm solution of ordinary ammonium molybdate, the latter becomes yellow, and, on cooling, deposits a crystalline precipitate, if the solution is not too dilute. If hydrochloric acid is added to a dilute solution even, there is an immediate precipitation of the silicomolybdate,

$$2(NH_4)_2O,SiO_2,12MoO_3,$$
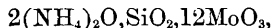
described by Parmentier. Part of the molybdate is converted, at the same time, into oxyfluormolybdate.

Ammonium silicofluoride can be substituted for hydrofluosilicic acid, and a precisely similar method yields titanomolybdates and zircono-molybdates.

Ammonium titanomolybdate, $2(NH_4)_2O,TiO_2,12MoO_3 + 10H_2O$, is obtained by adding ammonium titanofluoride solution to ammonium molybdate solution until the intensity of the yellow colour no longer increases, and then adding hydrochloric acid. It is completely insoluble in solutions of ammonium salts, but dissolves in water and in acids, and crystallises in small, yellow octahedra, which act strongly on polarised light.

Potassium titanomolybdate, $2K_2O,TiO_2,12MoO_3 + 16H_2O$, is an efflorescent salt, obtained in yellow prisms by adding potassium chloride to a hot concentrated solution of the preceding compound and allowing the liquid to cool.

Titanomolybdic acid, $TiO_2,12MoO_3,22H_2O$, crystallises in golden-yellow octahedra, melting at about 60°, and very soluble in water. It is obtained by adding hydrochloric acid to mercurous titanomolybdate, which is prepared from one of the preceding salts by double decomposition. A more rapid method is to agitate with ether an aqueous solution of the ammonium salt acidified with hydrochloric acid and allow the *heavy* ethereal solution to evaporate spontaneously.

Zirconomolybdates are obtained in a similar way and are strictly

analogous in composition. The ammonium salt crystallises with $10H_2O$ in yellow octahedra, and the potassium salt with $18H_2O$ in efflorescent, yellow prisms. C. H. B.

Action of some Metals on Acid Solutions of their Chlorides.
By A. DITTE and R. METZNER (*Compt. rend.*, 117, 691—694).—When a bar of tin is placed in a vessel containing a concentrated solution of stannous chloride in hydrochloric acid, on the top of which is a layer of water, crystals of tin rapidly form on the bar in the neighbourhood of the surface of separation of the two liquids. The system, as thus arranged, clearly consists of two identical electrodes immersed in two different liquids, and the two sources of electromotive force are the action of the acid on the tin and the diffusion of the acid into the supernatant water. If a bar of tin is placed simply in a hydrochloric acid solution of stannous chloride, no crystals are formed; if a thin layer of water is poured on the solution, it mixes with the subjacent liquid and becomes a conductor; if the layer of water is deep, it has its highest conductivity at the surface of separation, and the conductivity decreases gradually in a vertical direction as the upper surface of the water is approached. and, since the current traversing successive layers of the liquid diminishes in a similar manner, the size of the tin crystals shows corresponding variations, the deposit changing from well-defined crystals to a spongy, grey mass, and, finally, in the highest layers, to a very finely divided black powder.

Above the surface of separation, the bar of tin merely plays the part of the negative electrode, and can be replaced by any other conductor without any alteration in the phenomena. If, on the other hand, the metal rod or bar consists of two parts separated by some insulating material, and the latter lies on the surface of separation, no formation of crystals takes place until, by the progress of diffusion, the upper and lower parts of the rod are put into communication by two conducting liquids of different composition. The formation of the crystals is dependent on the action of the hydrochloric acid on the tin; no similar effect is produced by a solution of stannous chloride containing no free acid. It is also dependent on the energy developed by the diffusion of the acid into the supernatant water, neither cause alone being sufficient to electrolyse the stannous chloride.

Similar phenomena are observed with cadmium chloride and cadmium, the metal being attacked with difficulty by very dilute hydrochloric acid, but zinc, which is easily attacked by the dilute acid, does not give similar results. Nickel gives negative results, probably because the surface of the metal becomes polarised, and antimony and bismuth give negative results because they are not attacked by hydrochloric acid. C. H. B.

Solidification of Dilute Solutions of Antimony in Tin. By
F. W. KÜSTER (*Zeit. physikal. Chem.*, 12, 508—513).—Heycock and Neville (Trans., 1890, 376) were the first to point out that the solidifying points of dilute solutions of antimony in tin are higher than that of pure tin, a result which they explain by assuming the formation of solid solutions in these cases. The author shows that this is

most probably an instance of isomorphous mixture similar to those
which he has himself investigated (Abstr., 1890, 1209).   H. C.

**Action of Water on Disodium Platinum Thioplatinate. New.
Thioplatinum Salts.** By R. SCHNEIDER (*J. pr. Chem.*, [2], **48**, 411—
424; compare Abstr., 1892, 944).—When disodium platinum thio-
platinate, $2Na_2S,2PtS,PtS_2$ (*Annalen*, **138**, 618) is heated with
water, with exclusion of air, a deep-red solution and an insoluble
residue are obtained. The solution contains *sodium thioplatinosate*,
Na_2PtS_2, which, however, is speedily decomposed in accordance with
the equation $3Na_2PtS_2 + 4H_2O = 2H_2PtS_2,Na_2PtS_2 + 4NaHO$. The
insoluble residue consists of the salt *sodium platinum thioplatinate*,
$Na_2S,PtS,2PtS_2$, a microcrystalline, kermes-brown powder, which is
decomposed by air with the formation of sodium carbonate and plati-
num bisulphide, and by hydrochloric acid with liberation of the corre-
sponding acid, $H_2S,PtS,2PtS_2$.   A. G. B.

Mineralogical Chemistry.

Native Copper from Yunnan (China). By W. GOWLAND (*Chem. News*, **68**, 307).—A specimen of remarkably tough native copper, consisting of a flat, nodular nucleus, without crystalline structure, and weighing 208·6 grams, but encircled by incrusting layers of cuprite and green copper carbonates weighing 89·5 grams, was obtained from an outcrop in the province of Yunnan, China. The metal was found to be free from gold, lead, arsenic, antimony, bismuth, nickel, and cobalt, but to contain 0·028 per cent. of iron and 0·026 per cent. of silver; it being purer than the electrolytic copper at the author's disposal, a direct determination of copper was not made, but by difference the percentage of copper was found to be 99·946; it therefore surpasses in purity many specimens of native copper hitherto examined, and in fact may be classed with the Lake Superior and Chilian specimens.   D. A. L.

Nickel Arsenide. By E. WALLER and A. J. MOSES (*Jahrb. f. Min.*, 1894, i, Ref. 17, from *School of Mines Quart.*, **14**, 49—51).—The ore from a mine 18 miles from Silver City, New Mexico, consists of dendritic native silver, enclosed in a grey, brittle arsenide, which is found in a matrix of spathic iron ore. The hardness of the nickel compound is 5, its streak black, and its structure granular. Analysis gave results which, on the assumption that silica and silver were present as impurities, were as follows :—

As.	Ni.	Co.	Fe.
78·67	12·25	6·16	2·92

These results correspond with those demanded by the formula for

skutterudite, in which cobalt is replaced by nickel and iron. The authors, therefore, propose the name of *nickel-skutterudite* for this mineral.　　　　　　　　　　　　　　　　　　　　　　B. H. B.

Natural Oxides of Manganese. By A. GORGEU (*Bull. Soc. Chim.*, [3], 9, 650—661).—*Manganites.*—Four well-crystallised samples of manganite from Ilefeld (Hartz) gave analyses as follows :—

	SiO_2.	Fe_2O_3,Al_2O_3.	BaO.	PbO,CuO.	CaO.	K_2O,Na_2O.
I.	0·25	0·35	0·15	0·10	0·10	0·30
II.	0·45	0·25	0·30	0·10	0·20	0·20
III.	0·15	0·30	—	0·10	trace	0·15
IV.	0·05	0·25	—	0·05	0·15	0·25

	MnO.	O in excess.	H_2O.	Total.
I.	79·40	9·25	10·40	100·30
II.	79·35	9·40	10·10	100·35
III.	79·90	9·15	10·45	100·20
IV.	80·05	10·15	9·40	100·35

II has sp. gr. 4·34, hardness 3·5; III has sp. gr. 4·39, hardness 3·5.

The percentages of water, and of oxygen in excess of that required to form MnO agree with the formula, MnO_2,MnO,H_2O, excepting sample IV which appears to have begun to pass into pseudomorphic pyrolusite. The mineral is represented as manganous hydrogen manganite, because concentrated boiling nitric acid dissolves half the manganese on repeated treatment of the very finely powdered mineral.

Hausmannites.—Three samples from Ilmenau were examined; they each gave a red streak and appeared to be free from other oxides of manganese. The most noteworthy point is the presence of zinc oxide, not hitherto noticed excepting in the silicates, although the author has found 1—2 per cent. in diallogite form Dietz. The outer friable portion of sample I contained 8·30 per cent. of zinc oxide. Analyses gave :—

	SiO_2.	P_2O_5.	SO_3.	CO_2.	Fe_2O_3,Al_2O_3.	CaO.	MgO.	K_2O,Na_2O.
I.	0·30	trace	trace	trace	0·30	0·10	—	0·40
II.	1·45	0·05	0·10	0·15	0·70	0·55	0·45	0·20
III.	0·13	—	—	—	—	0·20		trace

	ZnO.	MnO.	O.	H_2O.	Total.
I.	8·60	83·40	7·05	0·05	100 20
II.	1·00	88·10	6·65	trace	99·40
III.	7·20	85·40	7·03	0·16	100·12

II has sp. gr. 4 77; III has sp. gr. 4·91, hardness 4·5—5.

Allowing for the oxide of zinc, concentrated nitric acid extracts two-thirds of the manganese; hence the formula of the mineral is $MnO_2,2RO$, where R represents Mn partly replaced by Zn.

Braunites.—Two well-crystallised specimens of braunite were analysed :—I from Saint-Marcel (Piedmont), hardness 6—6·5; sp. gr. 4·76; and II from Schwarzenburg, hardness 6·0; sp. gr. 4·83. No. I is the only oxide examined in which cobalt occurs.

	Gangue.	SiO_2.	MnO.	O.	Fe_2O_3.	CaO.	PbO,CuO.	CoO.
I.	2·80	9·40	74·68	7·50	3·80	0·50	0·15	0·30
II.	0·60	8·15	80·40	8·35	0·30	1·20	0·85	—

	MgO.	K_2O,Na_2O.	BaO.	P_2O_5.	H_2O.	Total.
I.		1·00	trace	0·05	0·20	100·30
II.	trace	0·20	0·20	—	0·20	99·65

These analyses indicate the formula $(MnSi)O_2RO$ for braunite, where SiO_2 partly replaces MnO_2 and R is chiefly manganese. Boiling dilute solutions of soda or potash have very little action on finely powdered braunite; hence silica is not present in the free state. As the mineral is completely decomposed by hydrochloric acid, rhodonite (SiO_2,MnO) is not present. Dilute nitric acid (1 : 9) has hardly any action on the Saint-Marcel braunites; hence tephroïte $(SiO_2,2MnO)$ is absent. Rammelsberg's formula, $SiO_2,MnO_2 + 2(MnO_2,2MnO)$, does not correspond with the above analyses.

The gangue has been deposited later than the main substance in each of the minerals examined, for the crystals show no evidence of penetration by the gangue, whereas the gangue surface corresponds with the projecting angles of the mineral crystals.   W. T.

Heintzite. By O. LÜDECKE (*Jahrb. f. Min.*, 1894, i, Ref. 19; from *Zeitschr. f. Naturw.*, 1892, 1—8).—The author admits that his heintzite from the pinnoite of Stassfurt (Abstr., 1891, 528), Feit's microcrystalline kaliborite from Schmidtmannshall (Abstr., 1892, 791), and Milch's hintzeïte (Abstr., 1891, 528) do not differ from one another. The composition of the three is $2K_2B_6O_{10} + 9MgB_4O_7 + 39H_2O$. Crystallographical measurements support this view. The name of heintzite has priority.   B. H. B.

Microchemical Investigation of Minerals. By J. LEMBERG *Jahrb. f. Min.*, 1894, Ref. 7; from *Zeit. deutsch. geol. Ges.*, 1892, 224—242).—The author describes various microchemical tests for distinguishing scapolite, hauyn, eudialyte, chabasite, and other minerals.   B. H. B.

Cordierite in an Eruptive Rock of South Africa. By G. A. F. MOLENGRAAFF (*Jahrb. f. Min.*, 1894, i, Mem. 79—91).—The rock described was obtained from the Cornelis River, near Harrismith, in the Orange Free State. It resembles most closely a diabase, and apparently forms a dyke in the Stormberg beds. Under the microscope, it is seen to be composed of glass in which crystals of spinel, cordierite, and augite occur. Analysis of the rock gave the following results.

SiO$_2$.	TiO$_2$.	Al$_2$O$_3$.	Fe$_2$O$_3$.	MgO.	CaO.	Na$_2$O.	K$_2$O,
64·54	0·79	19·16	7·23	3·39	2·47	0·57	1·13

These results correspond with those given by Osann for the cordierite-bearing mica andesite of Hoyazo. The South African rock increases the far from numerous examples of the occurrence of cordierite in eruptive rocks. B. H. B.

Melanite from Missouri. By E. HAWORTH (*Zeit. Kryst. Min.*, **22**, 428; from *Proc. Kansas Acad. Sci.*).—Melanite occurs in brownish-black crystals in cavities produced by solfataric action on a basic vein rock on the eastern fork of the Black River, Reynolds Co. The rock consists of triclinic felspar and green fibrous hornblende in a vitreous ground mass. Analysis of the melanite gave

SiO$_2$.	MnO.	Fe$_2$O$_3$.	Al$_2$O$_3$.	CaO.	MgO.	Total.
33·88	0·20	29·35	5·53	30·71	0·63	100·30

Its sp. gr. is 3·6. This is the first recorded occurrence of garnet in Missouri. B. H. B.

Iron Ore Deposit in North Sweden. By W. PETERSSON and H. SJÖGREN (*Jahrb. f. Min.*, 1894, i, Ref. 88—89; from *Geol. Fören. Förh.*, **15**, 45—63, 140—143).—The deposit described, known as the Routivare Iron Mountain, is situated about 9 miles from Quickjokk, in the Swedish province of Norrbotten. The ore (Analysis I) consists of titaniferous magnetite associated with green spinel, olivine, and talc. The rock (Analysis II) in which it occurs is a highly altered gabbro.

	SiO$_2$.	TiO$_2$.	Al$_2$O$_3$.	Cr$_2$O$_3$.	Fe$_2$O$_3$.	FeO.	MnO.	MgO.	CaO.
I.	4 08	14·25	6·40	0·20	33 43	34·58	0·45	3·89	0·65
II.	47·37	0·25	23·22	0·39	—	6·42	0·28	8·67	6·86

	K$_2$O.	Na$_2$O.	H$_2$O.	P$_2$O$_5$.
I.	0·15	0·29	1·32	0·016
II.	0·63	3·25	3·25	—

The mineralogical constituents of the ore are as follows. (1) Titaniferous magnetite, the main component; (2) ilmenite; (3) spinel; (4) olivine; (5) pyroxene; (6) chlorite; and (7), as accessory constituents, magnetic pyrites and apatite. B. H. B.

Diabase from Rio de Janeiro. By E. O. HOVEY (*Jahrb. f. Min.*, 1894, i, Ref. 80—81; from *Min. petr. Mitth.*, **13**, 211—221).—In the vicinity of Rio de Janeiro, numerous veins of diabase occur, whose width varies from a few inches up to 20 yards. The structure and character of these veins vary according to the thickness from the gabbro structure, with holocrystalline development in the widest, through the ophitic to porphyritic texture and hypocrystalline development in the narrowest. The author gives the results of analyses of the two extreme varieties. Augite occurs in two forms, namely, ordinary diabase-augite and augite resembling salite. A com-

parison of true salite from Sala, in Sweden, proves, however, that the salite-like augite of the diabase of Rio de Janeiro, New Haven, New Jersey, and Cape Blomedon is not salite.   B. H. B.

Sulphuretted Water from Alexeiewsk. By N. SAYTZEFF (*J. pr. Chem.*, **49**, 518—521).—Alexeiewsk is about 20 versts from Samara and 5 to 6 from Schmischlaewka. The mineral water is clear and colourless, and has a strong odour of hydrogen sulphide, a faintly saline taste, and a faintly acid reaction. On exposure to air, it becomes milky, through separation of sulphur, accompanied by a flocculent, black precipitate. The sp. gr. is 1·00141 at 14°. The temperature of the spring is 9·3°. The water contains in 10,000 parts

K_2SO_4.	Na_2SO_4.	$Na_2S_2O_3$.	$CaSO_4$.	$CaCO_3$.	$MgSO_4$.	$MgCl_2$.
0·1556	1·1302	0·1036	13·5843	2·7287	1·7706	0·2550

SiO_2.	Fe_2O_3.	SH_2.
0·1387	0·1083	0·1354

E. C. R.

Water and Sea-bottom Deposits from the Eastern Mediterranean. By K. NATTERER (*Monatsh.*, **14**, 624—673; compare Abstr., 1893, ii, 216).—The auther gives details of analyses of water and sea-bottom deposits, examined during the voyage of the ship " Pola " in the Eastern Mediterranean during 1893.   G. T. M.

Physiological Chemistry.

Respiratory Exchange. By A. MAGNUS LEVY (*Pflüger's Archiv*, **55,** 1—126).—This is a very complete account of experiments on animals and men, to show the effect of inanition and diets of different kinds —fats, carbohydrates, proteïd, bone, meat, mixed diet—on the respiratory interchanges. The calorimetric value of foods is also discussed. The methods of experiment are fully described. The most important result appears to be the absolute and relative increase of gas exchange and strength, if a proteïd diet is continued for some time.   W. D. H.

Absorption and Elimination of Hydrogen and Nitrous Oxide. By N. GRÉHANT (*Compt. rend. Soc. biol.*, 1893, 616—618).— A dog was allowed to breathe a mixture of hydrogen and oxygen (4 to 1) ; five minutes after, some blood was collected, and it was found that the nitrogen normally obtainable from blood was replaced by hydrogen ; in a few minutes this was replaced by nitrogen when the dog was allowed to breathe air again.

Another animal was allowed to breathe a mixture of 126 litres of nitrous oxide and 33 of oxygen. The blood gases obtained from 100 c.c. of blood amounted to 79·2 c.c., of which 42·8 was carbonic anhydride, 7·8 oxygen, 2·1 nitrogen, and 26·4 nitrous oxide. The

mixture did not produce anæsthesia, on account of the admixture with oxygen, as P. Bert showed. The animal was then allowed to breathe air, and the blood gases analysed at intervals; the quantity of carbonic anhydride and of oxygen fell and rose respectively to the normal, while the foreign gas rapidly disappeared, so that, in half-an-hour's time, none was left in the blood. W. D. H.

Pancreatic Ferments. By A. DASTRE (*Compt. rend. Soc. Biol.*, 1893, 648—651).—The experiments described show the independence of the two principal ferments contained in pancreatic juice, amylopsin, and trypsin. Three hypotheses are advanced as possible explanations; these are as follow :—

1. The amylolytic ferment is more soluble and diffusible than the proteolytic ferment, and so less firmly held by the glandular cells. The first macerations of the gland substance remove it almost completely.

2. The production of ferments by the pancreatic cell is successive; it is an operation of two acts, of which the first is the formation of amylopsin, the second of trypsin.

3. The two ferments are produced at the same time, but the tryptic one is in the condition of zymogen, only acquiring its fermentative activity after more prolonged contact with the products of the cellular activity of the gland. W. D. H.

Conversion of Maltose into Dextrose. By M. C. TEBB (*J. Physiol.*, 15, 421—432).—Dried pancreas, mucous membrane of the small intestine, Peyer's patches, lymphatic glands, salivary glands, liver, kidney, stomach, spleen, and striated muscle possess the power of converting maltose into dextrose. The relative activities are expressed in the following numbers :—The proportion of maltose to dextrose in similar specimens being for the intestine 1 : 3·21 ; for the spleen, 1 : 1·35 ; for lymphatic glands, 1 : 0·93 ; for the liver, 1 : 0·8 ; for Peyer's patches, 1 : 0·64 ; for the kidney, 1 : 0·66 ; for the stomach, 1 : 0·45 ; for pancreas, 1 : 0·31 ; for the salivary glands, 1 : 0·21 ; for muscle, 1 : 0·2. The small intestine is, therefore, the most active. Serum, bile (slightly), and Benger's pancreatic fluid (slightly) also act in the same way. Peyer's patches, to which Brown and Heron attributed a powerful action in this direction, are seen to be very feeble. W. D. H.

Action of Carbonic Anhydride on the Diastatic Ferments of the Animal Body. By W. EBSTEIN and C. SCHULZE (*Virchow's Archiv*, 134, 475—500).—The ferments investigated were the diastatic ferments of saliva, of the pancreas, blood-serum, muscle, kidney, and liver. In a neutral solution, carbonic anhydride hinders their activity; it appears to act like other weak acids in a corresponding degree of dilution, although in a few experiments with saliva a slight increase in its activity was noted.

In an alkaline solution, carbonic anhydride neutralises some of the alkali, and thus increases the activity of the ferment. In an alkaline solution of 0·021 per cent. sodium carbonate, or 0·015 per cent. disodium hydrogen phosphate, certain salts play the same *rôle* as

carbonic anhydride, neutralising the hindering action of the alkaline solution. The salts found in human blood-serum act thus, especially sodium chloride, and in a smaller degree, magnesium phosphate, $MgHPO_4$, also.

Acidity equal to 0·01 per cent. lactic acid stops the action of the diastatic ferments of the animal body.   W. D. H.

Influence of Chloroform on Artificial Gastric Digestion. By DUBS (*Virchow's Archiv*, **134**, 519—540).—Chloroform has been recommended by E. Salkowski (*Deutsch. med. Woch.*, 1888, No. 16) as a means by which organised ferments can be killed and the unorganised ferments left still active. Bertels (*Virchow's Archiv*, **130**), however, found that under certain circumstances chloroform hinders the activity of pepsin in artificial digestion mixtures. This question is taken up in the present paper with the following results :—Chloroform increases the activtity of pepsin in acid solutions in small doses, but hinders it in large doses; this appears to be due to the fact that large doses of chloroform precipitate pepsin. The same is true for hydrochloric acid extracts of the gastric mucous membrane, except that a greater concentration of chloroform (0·6 to 0·7 per cent.) is necessary to produce the harmful effect on the fermentative action. This difference depends on the presence of proteïd matter in the extracts of the mucous membrane. The harmful influence of passing a stream of air through the mixture is quite analogous.   W. D. H.

Source of Animal Heat. By M. RUBNER (*Zeit. Biol.*, **30**, 73—142).—This paper contains (1) a very complete dissertation on the various views held by physicists and physiologists as to the source of animal heat from the time of Lavoisier onwards ; (2) a description of the methods of animal calorimetry and of the special precautions taken in the present experiments ; (3) a full account of experiments on animals on different diets. The following table gives a summary of the results obtained.

Condition.	No. of days.	Total of the calculated heat production.	Total of the heat production by direct estimation.	Mean percentage difference.
Hunger .... {	5	1296·3	1305·2	} −1·42
	2	1091·2	1056·6	
Fed on fat	5	1510·1	1495·3	−0·97
Fed on meat and {	8	2492·4	2488·0	} −0·42
fat	12	3985·4	3958·4	
Fed on meat..... {	6	2249·8	2276·9	} +0·43
	7	4780·8	4769·3	

In the whole 45 days, the amount found by the calorimeter was only 0·47 per cent. less than that reckoned from the heat value of the food given. The food given is ultimately the only source of animal heat.

The close agreement between the heat production within and without the body is seen from the following numbers.

	Heat value of 1 gram of dry substance	
	Burnt in the body.	Burnt in Thompson's calorimeter.
Flesh (1)	4·059	4·000
„ (2)	4·007	4 000
Fat (1)	9·334	9·423
„ (2)	9·353	9·423

This is not surprising nor anything new in relation to fat; but with regard to meat, consisting as it does so largely of proteïd, the close correspondence of physical and physiological heat values is very noteworthy. W. D. H.

Lymph Formation during Muscular Work. By H. J. HAMBURGER (*Zeit. Biol.*, **30**, 143—178).—The composition of the lymph which flows from a lymph fistula in the neck of the horse is not quite constant. It is the proportion of water to solid constituents which chiefly varies; during the night, there is an increase of water due to diminished metabolism. One must, therefore, carefully distinguish between day and night lymph. After food, the lymph is increased in quantity three or four times; it is, therefore, necessary to distinguish between the lymph of rest and during or after feeding. Those constituents of the food, such as alkaline salts, which have a water-attracting power, appear to be especially potent in producing an increase in the quantity of lymph. The increase of lymph production cannot always be explained by rise of blood-pressure in the capillaries and veins, for if a horse is made to work, producing a fall of blood-pressure in the carotid, the lymph flows in greater quantity than when the animal is at rest, and the quantitative composition of the lymph of work is' different from that of rest, the percentage of solids falling, but the water-attracting constituents (chlorine and alkali) rising.

Even where increased flow of lymph and rise of blood-pressure go together, the first cannot be due to the second, as the composition of the lymph and of the blood-serum show no correspondence. This is against the filtration theory of lymph-formation.

Normal lymph has a much greater osmotic equivalent than the serum of the blood.

In a dead animal, clear lymph continues to flow from the fistula for 15 minutes or more. These facts are also against the filtration theory. It appears probable that the formation of lymph is due to the excitation of the capillary endothelium by the metabolic products of the tissues. W. D. H.

Elementary Composition of Ox Flesh. By P. ARGUTINSKY (*Pflüger's Archiv*, **55**, 345—365).—Flesh was dried, the fat and

glycogen being removed. The percentage composition of the residue, mean of five analyses, was as follows :—C, 49·6 ; N, 15·3 ; H, 6·9 ; O and S, 23·0 ; ash, 5·2 ; C : N, 3·24.　　　　　　　　　　W. D. H.

Formation of Sugar in the Liver.

By M. BIAL (*Pflüger's Archiv*, **55**, 434—468).—From a review of the literature of the subject, and from the author's own experiments, he draws the conclusion that the teaching of Claude Bernard on the *post-mortem* formation of sugar in the liver is amply confirmed. It is formed at the expense of the glycogen. Seegen considers that the sugar has its source in other substances, such as peptone ; but adequate reasons are given to show that this is not the case. Liver substance mixed with peptone solution never yields sugar.

The change of glycogen into sugar is further produced by a diastatic ferment, and this is believed to be the same as that found in the blood and lymph.

The fact that sugar is formed from glycogen does not, of course, exclude its possible formation from proteïd.　　　　　　W. D. H.

Asparagine in the Nutrition of Herbivora.

By H. WEISKE (*Zeit. Biol.*, **30**, 254—278).—Considerable discussion has occurred as to the part, if any, asparagine plays in nutrition, especially as to whether or not it is to be regarded as a proteïd-sparing food. The present contribution to the subject is grounded on experiments on rabbits. These show that asparagine exercises a good effect on the animals, that it probably does, under certain circumstances, act as a proteïd-sparing food, but that its beneficial effect may be, in part, due to its action on the digestive apparatus ; it certainly appears to favour the digestion of starch.　　　　　　　　　　　W. D. H.

Substance resembling Strychnine in the Muscles of Tetanised Animals.

By J. COURMONT and M. DOYON (*Compt. rend. Soc. Biol.*, 1893, 714—715).—Muscle rendered tetanic by subcutaneous injection of the soluble products of the Nicolaier's bacillus (after a constant period of incubation) contains a substance which, like strychnine, produces contraction without incubation. This substance can be extracted from the muscles by means of water, and the aqueous extract produces symptoms resembling those caused by strychnine. This substance is considered to be the cause, not the result, of the muscular contraction.　　　　　　　　W. D. H.

Estimation of Proteïds and Extractives in Cow's and Human Milk.

By I. MUNK (*Virchow's Archiv*, **134**, 501—519).—The amount of proteïd in milk is most rapidly and accurately obtained by estimating, according to Kjeldahl's method, the amount of nitrogen contained in the precipitated proteïd. After precipitation of the proteïd by alcohol, from one-fifteenth to one-thirtieth of the proteïds of cow's milk remain in solution. Tannin and copper hydroxide (at the boiling temperature) precipitate the proteïds entirely, and of the two precipitants the copper method is recommended as the more rapid. Fresh cow's milk contains, in 100 parts, 0·022 to 0·034 part of extractive nitro-

gen; human milk, 0·014—0 026 part. The proportion of extractive nitrogen to total nitrogen is 1 : 16 in cow's milk; 1 : 11 in human milk.

If the total nitrogen in milk is determined by Kjeldahl's method, sufficient accuracy is usually obtained for the proteïd nitrogen by multiplying the total nitrogen by 0·94 and 0·91 in cow's and human milk respectively.

The precipitated proteïds consist of caseïn, albumin, and globulin; the ash free product contains 15·76 per cent. of nitrogen. If the nitrogen found by Kjeldahl's method is multiplied by 6·34, the amount of proteïd is obtained. Sebelien gives the multiplier as 6·37 (Abstr., 1889, 450). W. D. H.

Human Bile. By O. 'HAMMARSTEN (*Kön. Ges. der Wiss. Upsala*, Separat-abzug, 1893).—This paper contains careful analyses of human bile. The principal new point is that the mucin is true mucin, not nucleo-albumin, as in in ox-bile. W. D. H.

Work of the Kidney. By W. H. THOMPSON (*J. Physiol.*, **15**, 433—448).—A full account of experiments of which a preliminary statement has already been made (Abstr., 1893, ii, 542).
W. D. H.

Elementary Composition of Dog's Urine on Flesh Diet. By F. MEYER (*Pflüger's Archiv*, **55**, 212—229).—After allowance is made for the ash. the following table gives the percentage elementary composition of the organic material in the urine at different periods.

	6¼ hours after meal.	Fasting condition.	7 hours after meal.	24 hours urine.	Mean.
C	23 ·40	21 ·60	22 ·51	22 ·05	22 ·5
H	6 ·91	6 ·73	6 ·67	6 ·70	6 ·8
N	39 ·02	39 ·57	39 ·74	39 ·66	39 ·4
O	30 ·67	32 ·10	31 ·08	31 ·59	31 ·3
C:N	0 ·60	0 ·55	0 ·57	0 ·56	0 ·57

W. D. H.

The Ferrocyanide Test for Urine. By J. P. KARPLUS (*Chem. Centr.*, 1893, ii, 496; from *Centr. klin. Med.*, **14**, 577).—In testing urine for albumin by means of potassium ferrocyanide and acetic acid, a yellow coloration is frequently observed, for which no explanation has hitherto been given. As it was not improbable that the reaction might be due to the presence of nitrites, the author has examined a large number of samples of urine from healthy and diseased persons, and finds that when quite fresh none of these contain nitrites, but that when the urine has remained for periods of upwards of 24 hours, the presence of nitrites may frequently be detected.

Fresh urine from jaundice patients was found to contain no nitrites, but 6 out of 12 samples which had been kept became green on addition of acetic acid, and all these, after removal of the bile pigments, gave the nitrite reaction. In testing for biliprasin in such urine, the

absence of nitrites must, therefore, first be proved. In the urine of patients taking sodium iodide, free iodine occurred together with nitrites.

The urine bacterium recently described by the author has, in addition to its action in forming hydrogen sulphide and probably methylic mercaptan, the property of reducing nitrates to nitrites.

H. G. C.

Metabolism in Fever. By R. MAY (*Zeit. Biol.*, **30**, 1—72).—The development of heat is increased in the febrile condition; this depends, during hunger, on an increased decomposition of proteïd, but it can be lessened by the administration of carbohydrates.

Glycogen disappears in fever more rapidly than at the normal body temperature. The ratio N : C is altered in the urine of fever, febrile urine being richer in carbon.

The increased proteïd metabolism in fever is, in the chief place, due to the increased need of the organism for carbohydrates. The degeneration of the cells in causing an increased output of nitrogen is only of secondary importance.   W. D. H.

Chemical Composition of a Lipoma. By O. SCHULZ and G. SCHWALBACH (*Pfluger's Archiv*, **55**, 231—239).—The fatty tumour investigated contained 22 per cent. of water, 2·25 of connective tissue, 75·75 of fat. The fat contained 7·31 per cent. of free fatty acids and 92·69 of neutral fats. After saponification, 100 grams of the fat yielded 94 grams of fatty acids, and 9·9 grams of glycerol. In the fatty acid mixture the amounts per cent. present were : Oleïc acid, 65·57 ; stearic acid, 29·84 ; and palmitic acid, 4·59. Cholesterol was present in appreciable quantity.   W. D. H.

Physiological Action of Pentoses. By W. EBSTEIN (*Virchow's Archiv*, **134**, 361—363; compare Abstr., 1892, 1506, and 1893, ii, 427).—A further contribution to the polemical aspect of this subject, in answer to criticisms raised by Cremer.   W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Tuberculin. By W. KÜHNE (*Zeit. Biol.*, **30**, 221—253; compare Abstr., 1893, i, 233).—Koch's purified tuberculin contains about 10 per cent. of proteïd matter, and it is to this and the changes it undergoes under variations of culture, that the present communication chiefly relates. The separation of the proteïds from one another by neutral salts was similar to that usually adopted, and the properties and tests for each are fully described. There were found (1) an albuminate ; (2) special albuminoses, for which the name *acro-albumoses* is proposed; (3) a deutero-albumose; and (4) traces of peptone. About one-fifth of the solid matter present is mineral in nature. Koch's tuberculocidin appears to contain small quantities of

the same substances; but, if these are removed by alcohol, the substance is not rendered wholly inactive. W. D. H.

Presence of a Diastatic Ferment in Green Leaves. By S. N. VINES (*Ann. Agron.*, 19, 555; from *Annals of Botany*, 5, 409—412).— Wortmann, not finding a diastatic ferment in green leaves, in which, nevertheless, saccharification of starch is very active, attributed saccharifying power to the living protoplasm itself. The author cites the following experiment to prove that leaves do contain a certain quantity of diastase. 500 grams of grass were crushed in a mortar with 500 c.c. of water, and the liquid allowed to remain for four hours, after which six mixtures were made, thus:—(1) 50 c.c. extract and 50 c.c. thin starch paste; (2) the same, but subsequently boiled; (3) the same, but with a little thymol added; (4) the same, but with 5 grams of boric acid added; (5) 50 c.c. of extract and 50 c.c. of distilled water; (6) 50 c.c. of starch paste and 50 c.c. of distilled water.

On the following day, the reducing sugar present in each solution was determined by Fehling's solution, when the following amounts of sugar, in grams per 100 c.c., were obtained: (1) 0·793; (2) 0·450; (3) 0·740; (4) 0·690; (5) 0·444; (6) none.

It appears, by comparing Nos. 2 and 5 with No. 1, that about 0·34 gram of sugar was formed by the action of the diastase in the green grass. J. M. H. M.

Soluble Ferments secreted by Aspergillus niger and Penicillium glaucum. By E. BOURQUELOT (*Compt. rend. Soc. biol.*, 1893, 653—654).—These moulds, grown in Raulin's liquid, secrete a large number of soluble ferments; thus in *Aspergillus*, a diastase, an invertin, a maltase, a trehalase (found also in several other fungi), an inulase, and an emulsin (in small quantities) were found. In *Pencillium*, there were found the same, some in only small proportions; emulsin, however, is not mentioned as being present. It is added that, in certain conditions of culture, proteolytic ferments are also formed. W. D. H.

Non-organised Active Proteïd Material. By T. BOKORNY (*Pflüger's Archiv*, 55, 127—142).—Inactive proteïd is the storage proteïd used in the nutrition of growing plants. The term active proteïd is applied to that in the cell protoplasm, and it is termed non-organised, as it occurs there in granules (proteosomes). A large number of plants were investigated by microscopic and microchemical analysis. The proteïd nature of the granules is readily demonstrable by these means. Their behaviour towards ammonia and caffeïne distinguishes them from ordinary non-living albumin, which is indifferent to these reagents; they also show the power of reducing silver salts. The substance is considered to play the part of reserve material for the growth of cells and organs. W. D. H.

Evolution of Free Nitrogen during the Fermentation of Horse Excrement. Influence of Urine on the Formation and Volatilisation of Ammonia during the Fermentation of Solid

Animal Excrement. By S. JENTYS (*Bied. Centr.*, **22**, 801—803; from *Bull. Akad. Sciences de Cracovie*, 1892, 303 and 310).—The results of the author's experiments indicate that a loss of nitrogen may occur during the fermentation of horse excrement. The conditions on which this loss depends are unknown, but there is some reason to suppose it to be due to specific organisms, especially as there are microbes which are known to liberate nitrogen from its compounds. It seems certain that the nitrogen evolution does not depend on the presence of previously formed nitric acid, inasmuch as in this case there would be a greater evolution in absence of oxygen.

The presence of urine does not seem to be favourable to change in the nitrogen compounds of the solid excrement. The loss of ammonia in the mixed excrement is greater the larger the proportion of urine present. Decomposing solid excrement hinders, to some extent, the evolution of ammonia, which becomes fixed, partly by acids and partly by microorganisms. It is possible that the dilution of the urine has some effect on the loss of ammonia.   N. H. M.

Exchange of Carbonic Anhydride and Oxygen between **Plants and Air.** By T. SCHLOESING, jun. (*Compt. rend.*, **117**, 756—759 and 813—816; compare Abstr., 1893, ii, 180).—The method of experiment which has been already described (*loc. cit.* and *Ann. Inst. Pasteur*, January, 1893) consisted in growing the different plants in quartz sand in enclosed vessels under conditions which enabled measured amounts of gases to be introduced and removed. Excess of oxygen was absorbed by means of heated copper. Check experiments without plants were made for each series of experiments.

	Carbonic anhydride.			Oxygen.			CO₂ disappeared, O₂ liberated = 1.
	Initial.	Final.	Loss.	Initial.	Final.*	Gain.	
1. Flax	1468·0	71 0	1397·0	978·9	2529·6	1550·7	0·90
2. Peas	1592·8	790·0	802·8	930·1	1778·3	848·2	0·95
3. White mustard..	3015·5	179·4	2836·1	852·1	4115·0	3262·9	0·87
4. „ „ †.	3707·4	583·4	3124·0	855·8	4415·3	3559·5	0·88
5. Algæ...........	477·8	66·3	411·5	228·8	761·2	532·4	0·77

In the first series a gain of 8 c.c. of carbonic anhydride and a loss of 12 c.c. of oxygen were observed; in the second series losses of 10·3 and 9·7 c.c. of carbonic anhydride and oxygen respectively. These errors are taken into account in the table of results given above.

The peas did not grow well for want of sufficient nitrogen, not having been microbe-seeded.

* Including amounts absorbed by copper.
† Sodium carbonate mixed with soil.

As a check, the carbon supplied in soil, in seeds, and in the carbonic anhydride was estimated, as well as the final amounts in soil, plants, and carbonic anhydride recovered. The results were as follows :—

Experiment.	1.	2.	3.	5.
C at commencement....	834·4	1088·8	1687·9	265·6
C at conclusion	787·0	1090·3	1648·1	256·9
Difference	−47·4	+1·5	−39·8	−8·7

The losses in Experiments 1 and 3 are probably due to absorption by the glass, which was always very alkaline. Assuming this to be the case, and applying the correction, the relations $CO_2 : O_2$ would become for (1) 0·84 and for (3) 0·85.

In the case of Experiment 5 with algæ (mainly *Protococcus vulgaris*, with *Chlorococcum infusionum, Ulothrix subtilis*, and *Scenedesmus quaaricauda*) the following nitrogen results are given :—Nitrogen gas introduced 863·1 c.c., extracted 863·3 c.c. ; gain = 0·2 c.c. The indirect method, in which the initial amounts of nitrogen gas, nitrogen in the soil and in the nutritive solution, and the final amount as gas and in soil and algæ together were determined, gave identical results, namely, 1107·7 milligrams of nitrogen. N. H. M.

Chemical Nature of Cytoplasm and Cell Nucleus. By E. Zacharias (*Chem. Centr.*, 1893, ii, 461 ; from *Ber. deutsch. Bot. Zeit.*, 11, 293).—The author regards the following points as proved with regard to the distribution of proteïd compounds in the cells : the cell protoplasm and cell nucleus consist to a large extent of substances which are insoluble in artificial gastric juice, the greater proportion of these being the chromatin substances of the cell-nucleus (nucleïn). In their reactions, the latter agree with the undigested portion of the salmon spermatozoa from which Miescher prepared nucleïc acid. The other insoluble portions show different reactions, and are classed together by the author under the name *plastin*.

The cell protoplasm and cell nucleus contain in addition proteïds soluble in the digestive fluid, the nucleoli being in many carefully-examined cases especially rich in these substances, whereas cell protoplasm, especially in fully-grown plant cells, frequently contains them in but small quantity. H. G. C.

Carbohydrates of the Fruit of the Kentucky Coffee Nut Tree (Gymnocladus canadensis). By W. E. Stone and W. H. Test (*Amer. Chem. J.*, 15, 660—663).—The fruit consists of a leathery pod from 3 to 10 in. in length, and contains from two to six brown, oval, and very hard seeds embedded in a greenish, waxy pulp or gum. This gum has a sweet but very disagreeable taste, and at the time of ripening is soft and easily removed, although later it becomes horny. It contains no galactose, galactan, or starch, but abundance of soluble reducing sugars and pentosans.

The alcoholic extract yielded cane sugar (15 per cent.), $[\alpha]_D = $ ·65·4°, and glucose (15 per cent.).

The gummy residue, on hydrolysis with dilute sulphuric acid,

yielded an insoluble substance resembling cellulose, and a thick, reducing syrup which gave the furfuraldehyde reaction for pentoses. The osazone melted at 175—180°, indicating a mixture. This was separated by means of alcohol and water into two fractions : the first proved to be glucosazone (m. p. 204—205°), soluble in alcohol but insoluble in boiling water ; the second (m. p. 153°) was probably arabinosazone (m. p. 158—160°), insoluble in alcohol but soluble in boiling water. The latter gave abundance of furfuraldehyde when boiled with strong hydrochloric acid, and its alcoholic solution was optically inactive, so that it was not xylosazone. The glucose and arabinose probably exist in the original gum in combination as *gluco-araban.*   JN. W.

Sugar from Apple Pectin. By R. W. BAUER (*Landw. Versuchs-Stat.*, **43**, 191).—Apple pectin, extracted with alcohol, was boiled for four hours with 0·5 per cent. sulphuric acid, filtered, and polarised, when a rotation of +17° was observed. The filtrate, treated with an equal volume of alcohol, became clear after being kept for a year, and had an agreeable odour of ethylic malate. After neutralising with baryta, and evaporating the filtered solution under diminished pressure over sulphuric acid until of constant weight, a substance (2·763 grams) was obtained which proved by its optical properties ($[\alpha]_D = +18·77°$) and its osazone (microscopic, gold-coloured needles melting at 170°) to be xylose, produced by hydrolysis from xylan present in apple pectin.   N. H. M.

Formation of Pectin by the Action of Lime on the Sugar-Cane. By H. C. P. GEERLIGS (*Chem. Centr.*, 1893, ii, 531 ; from *Arch. Java Suikerindustrie*, 1893).—The pectin which is always found in the juice of the sugar-cane during the manufacture of sugar is formed by the action of lime on the fragments of the cane which are present. Its formation may be prevented by carefully filtering off the latter, or it may be precipitated with barium chloride in alkaline solution.

The crude wax of the sugar-cane may be purified by recrystallisation from alcohol, and then forms white, crystalline plates melting at 82°, and boiling at 146° [?]. Unlike other waxes, it does not consist of ethereal salts of fatty acids, but is chiefly composed of a saturated alcohol having the formula $C_{24}H_{25}O$ [?] ; the latter, on distillation with soda lime, yields a hydrocarbon melting at 92°, and boiling at 225°. Dumas and Leroy have recently obtained similar results in the case of American sugar-cane wax.

When the syrup from the centrifugals is heated by live steam, a thick froth is formed which may readily be removed, and which otherwise adheres to the sugar, crystallising out on direct evaporation. It has approximately the same composition as the syrup, but contains rather more ash and fat. The froth can only be obtained from a purified syrup to which these impurities have been added, by mixing with them a little bicarbonate, from which it would appear that the evolution of gas is necessary for its formation. In the crude syrup this is probably brought about by the carbonic anhydride evolved in the decomposition of the glucin present.
                                                       H. G. C.

Occurrence and Detection of Indican in Plants. By H. MOLISCH (*Chem. Centr.*, 1893, ii, 667—668 ; from *Zeit. Österr. Apoth. Verein*, **31**, 524).—Indican only occurs in about 10 phanerogamous species of the vegetable kingdom. Whether a plant contains indican can be rapidly decided by the following test :—Fragments of the plant are boiled for about half a minute in a test tube with 2 per cent. ammonia solution, filtered over a platinum cone, and extracted with a little chloroform. A similar experiment is carried out with **2** per cent. hydrochloric acid. In the presence of indican, one or both of the chloroform extracts is coloured blue. Indican may occur in many of the organs and tissues of the indigo plants, but is mainly found in the foliage leaves. The statements found in the literature of the subject that indican occurs in *Mercurialis perennis*, *Melampyrum arvense*, *Polygonum Fagopyrum*, *Phytolacca decandra*, *Monotropa Hypopitys*, *Fraxinus excelsior*, *Coronilla Emerus*, and *Amorpha fructiosa*, are inaccurate. A chromogen does occur in the organs of the fresh toothwort (*Lathræa Squamaria*), which yields a blue colouring matter with dilute hydrochloric acid ; but this is quite distinct from indigo. A. H.

Amount of Maltose and the Fermentability of Wort and other Extracts. By O. REINKE (*Bied. Centr.*, **22**, 839—840).— Malt dried at 80° contained water (5 per cent.), and extract (73·15 per cent.) yielding 70 per cent. of maltose and 17 per cent. of dextrin after inversion and deduction of the maltose. When very lightly dried, the maltose was 5 per cent. higher and the dextrin 5 per cent. lower. In highly-dried malt, the amounts of maltose and dextrin were respectively 7 per cent. lower and 7 per cent. higher. 90 per cent. of the maltose fermented at 30°.

As regards extracts for the manufacture of spirit, the following percentage results are given for sweet potato extracts :—

	1.	2.	3.	4.
Maltose in extract....	64·84	67·16	60·60	68·09
Dextrin in extract....	14·04	13·46	14·41	15·90
Fermentable maltose..	58·36	60·44	54·54	61·28
In the filtrate :				
Saccharimeter° Ball ..	25·00	20·80	25·10	17·3
Maltose.............	16·21	13·97	14·00	11·78
Fermentable maltose..	14·59	12·57	12·6	10·6
Dextrin.............	3·51	2·80	4·02	2·75

When the fermentation is complete, there is generally only 6 per cent. of dextrin left. When the 90 per cent. of fermentable maltose is calculated as dextrose, and the amount of dextrose corresponding with half the dextrin added, and the whole multiplied by 64·64, the result gives the amount of alcohol to be obtained from the extract.
N. H. M.

Composition of Seeds and Etiolated Sprouts of Hemp (Cannabis sativa) and of Sunflower (Helianthus annuus). By S. FRANKFURT (*Landw. Versuchs-Stat.*, **43**, 143—182).—A qualitative examination, the details of which are given, showed the presence

of the following compounds in hemp seeds :—Proteïds, nucleïn, and other indigestible nitrogenous compounds, organic bases, lecithin, cholesterol, glycerides, cane sugar, non-crystalline soluble carbohydrates, hemicellulose, citric acid, cellulose, pentosan, and mineral matters. Detmer failed to find soluble carbohydrates in the seeds (*Physiol. Chem. Untersuchung über d. Keimung ölhaltigen Samen*, p. 38). The quantitative results are next given (per cent.).

Proteïds.	Nucleïn, &c.	Lecithin.	Cholesterol.	Glycerides and free fatty acids.
18·63	3·36	0·88	3·07	30·92

Cane-sugar and other soluble carbohydrates.	Crude fibre.	Soluble organic acids.	Ash.	Not determined.
2·59	26·33	0·68	5·551	11·03

As regards the changes which take place during germination, Detmer (*loc. cit.*) showed that the fat diminishes in amount, and is replaced by starch, cellulose, &c. Owing to the difficulty of obtaining large enough quantities of sprouts, the author only made a quantitative examination for certain constituents. Asparagin and two compounds, probably glutamic and glyoxylic acid respectively, were found.

The sunflower seeds and sprouts were more thoroughly investigated. The seeds were separated from the shells, and the two portions, which had the relation 53·6 : 46·4, separately examined. The percentage composition was found to be as follows :—

	Seeds without shell.	Shells.	Whole seeds.
Proteïds	24·06	1·33	13·50
Nucleïn, &c..................................	0·96	—	0·51
Lecithin	0·44	—	0·23
Crude fat	55·47	1·00	30·19
Cane sugar and other soluble carbohydrates	3·78	—	2·13
Crude fibre..................................	2·24	64·54	31·14
Soluble organic acids	0·56	—	0·30
Ash	3·66	1·93	2·86
Not determined	8·83	31·20	19·14

The seeds freed from shells contain also pentosan (soluble, 0·87; insoluble, 1·87 per cent.). They contain no, or almost no, hemicellulose. The shells are very poor in nitrogen. They contain hemicellulose. When the shells are kept in contact with 0·5 per cent. soda for a day, and the residue washed and boiled with 2 per cent. sulphuric acid, a sugar was obtained which, when isolated, proved to be xylose.

The quantitative examination of the etiolated sunflower sprouts showed the presence of asparagine and glutamine, malic acid, and considerable amounts of soluble carbohydrates. Nitrogenous organic bases were present only in very small amounts. Cane sugar, cellulose, hemicellulose, and pentosans were also found. The

percentage composition of the dried sprouts freed from shells was as follows :—

| | | Asparagine and | | | Cane sugar, |
Proteïds.	Nucleïn, &c.	glutamine.	Lecithin.	Fat.	&c.
15·00	4·56	4·05	0·85	24·54	14·75

Soluble organic acids.	Crude fibre.	Ash.	Not determined.
2·43	11·52	4·09	18·21

In order to compare the composition of the seeds with that of the sprouts, the quantities were calculated on the assumption that the amount of ash in both is practically the same. The results show first a great diminution in the amount of proteïds, whilst the insoluble nitrogen compounds (nucleïn) increased considerably (0·96 to 4·05). Unlike the etiolated sprouts of vetches and lupins, which contain considerable quantities of nitrogenous organic bases, the sunflower sprouts contained a very small amount. Another difference is the increase of lecithin (0·44 to 0·71 per cent.). Schulze observed a loss in lupins and vetches. The percentage of fat became much lower during germination, whilst the soluble carbohydrates increased. There was no loss of nitrogen during germination.   N. H. M.

Development and Maturation of Cider Apples. By L. Lindet (*Compt. rend.*, **117**, 696—698).—Apples were taken every two weeks (from 24th July to 3rd November) from the same tree and analysed. The average weight of the apples at each date was as follows :—(1) 24th July, 21·5 ; (2) 7th August, 34·0 ; (3) 23rd August, 46·0 ; (4) 7th September, 50·2 ; (5) 21st September, 60·3 ; (6) 4th October, 68·7; (7) 18th October, 75·3; and (8) 3rd November, 76·5 grams. The percentage composition of the apples at the different dates was :—

| | | Invert | | Cellulose | Nitrogenous | |
	Starch.	Saccharose.	sugar.	Acidity.	substance.	matter.	Ash.
1.	4·8	1·1	6·4	0·5	4·4	—	0·4
2.	4·8	1·2	6·8	0·5	3·1	0·6	0·4
3.	4·9	1·2	8·3	0·4	3·2	0·5	0·4
4.	5·8	2·3	8·3	0·4	2·8	0·3	0·3
5.	3·8	2·5	8·3	0·3	2·8	0·3	0·3
6.	3·3	3·2	8·2	0·2	2·7	0·3	0·2
7.	2·1	3·7	8·6	0 2	2·6	0·4	0·3
8.	0 8	2·9	9·4	0·2	—	0·3	0·2

The apples were green until September 7, at which date the pips began to become coloured. The chief change is in the starch, which, as ripening proceeds, becomes converted into what seems to be a mixture of saccharose, glucose, and levulose. It is possible that a portion of the saccharose had migrated from the leaves, but it is probable that some of it is furnished by the starch. The same disappearance of the accumulated starch, and, coincidently, an increase of saccharose and invert sugar was also observed in apples allowed to ripen after being taken from the tree.   N. H. M.

Nitrification of Prairie Soils. By J. DUMONT and J. CROCHE-
TELLE (*Compt. rend.*, **117**, 670—673).—Boussingault, and more
recently Bréal, have shown that prairie soils contain comparatively
small amounts of nitrates, so that the enormous amount of organic
nitrogen becomes very slowly available for vegetation. It seemed
likely that the slow nitrification is due to insufficient alkalinity. The
authors accordingly instituted experiments in which two different
soils (containing respectively 6·84 and 5·76 per cent. of humus) were
exposed for three or four weeks, after being treated with various
amounts (0·1 to 1·0 per cent.) of potassium carbonate, chloride, and
sulphate, and sodium carbonate (each alone); check experiments were
made in which nothing was added. At the conclusion of the experi-
ments the soils were extracted, and the nitric acid estimated. Similar
experiments were made in which arable soils (containing 2·9 and 1·08
per cent. of humus) were treated with the various salts, and exposed
for 15 days.

The results of the experiments show that with the rich soils an
addition of 0·2 to 0·3 per cent. of potassium carbonate increases
nitrification, whilst larger quantities are injurious. Potassium sulph-
ate (0·7 to 0·8 per cent.) gave rise to increased nitrification.
Potassium chloride had only a slight effect, the nitric nitrogen per
cent. being raised from 0·008 per cent. to 0·01 per cent. with 0·025
to 0·3 per cent. of the salt. Sodium carbonate had no beneficial
effect, nitrification being lessened when more than 0·15 per cent. was
applied to the soil.

In the case of the experiments with arable soils, in which only one
amount of each salt was applied (0·2 per cent.), the best result was
obtained with potassium sulphate. It remains to be ascertained what
amount of the salt gives the best results.   N. H. M.

Comparative Experiments with various Phosphates. By
O. KELLNER, Y. KOZAI, Y. MORI, and M. NAGAOKA (*Landw. Versuchs-
Stat.*, **43**, 1—14).—Experiments have already been made on the effect
of different phosphates on irrigated soil (*ibid.*, **41**, 305). The results
now given were obtained on ordinary arable land, consisting, like the
irrigated soil, of sand mixed with volcanic ashes, rich in easily de-
composable aluminium silicates, iron, and humus, but containing very
little lime. The manures employed were double superphosphate
(with 47·84 total and 43·65 per cent. of phosphoric acid, soluble in
water), precipitated calcium phosphate (with 29·35 total phosphoric
acid), basic slag (with 21·75 per cent. of phosphoric acid), steamed
bone meal (with phosphoric acid, 23·06; nitrogen, 3·87; and fat, 1·33
per cent.), crude bone meal, freed from fat (phosphoric acid, 19·70;
nitrogen, 4·74; and fat, 1·93 per cent.), crude crushed bone (phos-
phoric acid, 21·66; nitrogen, 4·61; and fat, 14·07 per cent.) and bone
ash (containing 30·465 per cent. of phosphoric acid). The experi-
ments were conducted in Wagner's zinc cylinders, 60 cm. in diameter,
and 1 m. deep. Calcium carbonate (1000 kilos. per hectare),
potassium sulphate (200 kilos. per hectare) and ammonium sulphate
(containing 50 kilos. of nitrogen per hectare) were mixed with the
soil as well as the phosphates, which were each applied in two

quantities, 50 and 100 to 100 and 200 kilos. per hectare. There were 48 cylinders, six without phosphate and six with each manure (three with the smaller and three with the larger amount). Barley was first sown. After the plants were cut and the stubble mixed with the soil, millet was sown, next wheat, and lastly buckwheat. The total dry substance, and the amount of phosphoric acid removed from the various cylinders is given in tables. The larger amounts of manures gave in every case higher yields than the smaller, but as they did not in every case have their full effect, the results obtained with the smaller quantities are the more suitable for comparison. Taking first into consideration the effect on the first growth (barley), superphosphate gave the highest yield of dry produce, which contained 21·5 per cent. of the total phosphoric acid applied. The next most efficacious manure was steamed bone meal, of which 16·6 per cent. of the total phosphoric acid applied was found in the produce. Then precipitated calcium phosphate, crude bone meal free from fat, crude crushed bone, basic slag, and, lastly, bone ash. The produce obtained under the influence of these manures contained respectively 13·8, 12·4, 12·6, 13·1, and 5·0 of the total phosphoric acid applied. It is noteworthy that the high percentage of fat in the crushed bone (14·07) did not hinder the utilisation of the phosphates.

As regards the effect of the manures on the subsequent growth (millet, wheat, and buckwheat), there was a decided but different effect in each case. The results, which are shown in a curve, indicate a great similarity in the after-effect of the superphosphate, the steamed bone meal, and the precipitated phosphate and also the basic slag, all of which were chiefly utilised by the first two growths. The slight effect produced by the superphosphate and the precipitated phosphate in the after-growths was due to their diminished solubility in contact with the soil, but better results were expected with basic slag. Both the crude bone meal and the crushed bone, which had but little influence on the first crop, had very considerable effect on the succeeding crops, and their action would probably have continued long.

Of the different bone manures applied, the crude crushed bones gave the greatest total yield; next the bone meal freed from fat; and lastly, the steamed bone meal. The results show that, under the prevailing climatological conditions, fat also acts in unlocking the calcium phosphate, although more slowly than the nitrogenous matter.

Bone ash becomes gradually and uniformly available for the roots. It is not suitable for damp rich soils.   N. H. M.

Analytical Chemistry.

An Automatic Extractor. By W. D. HORNE (*Chem. News*, **68**, 250).—The following arrangement is devised to effect the delivery of a definite quantity of water in portions of equal volume at regular intervals. A bottle of the desired capacity is fitted with a stopper,

bored with two holes, each carrying an open tube; the tubes pass just through the stopper internally, but externally one of them is short and straight, and terminates with a constricted orifice, whilst the other is bent twice at right angles, and extends down the whole height of the bottle outside. In use, the bottle is filled with water, stoppered, and inverted, and water can then be caused to escape from the short tube at any desired rate by regulating the supply of air admitted through the other tube. This regulated water supply drops into a receptacle suspended below the bottle, and provided with an adjustable inverted siphon inside, by which any required volume of water can be automatically drawn off at a time, and utilised for washing a precipitate or other purpose.　　　　　　　　　　　　D. A. L.

Lunge's Gas Tables. By A. LWOFF (*Zeit. angw. Chem.*, 1893, 443—445).—In Lunge's original tables, a correction for pressure down to 710 mm. is given. The author has now also corrected the volumes for pressures varying from 680 to 710 mm.　　　L. DE K.

Indicators for Titrations with Standard Sulphide Solutions. By P. WILLIAMS (*Chem. News*, **68**, 236).—The author has compared the delicacy of the following reagents when used as indicators for titrations with standard sulphide solutions :—I. A solution of sodium tartrate, treated with a small quantity of caustic soda and lead acetate, and heated until clear. II. A solution of potassium nitroprusside, saturated with soda, evaporated nearly to crystallising, and treated with 4 parts of alcohol, and filtered. With the first reagent 0·0000245 gram, with the second 0·0000982 gram of sodium sulphide in 1 c.c. may be detected.　　　　　　　　　　D. A. L.

Estimation of Dissolved Oxygen in Water. By C. M. VAN DEVENTER and B. H. JÜRGENS (*Chem. Centr.*, 1893, ii, 546; from *Maandbl. natuurw.*, **18**, 72).—The method described depends on the fact that when iodine is set free from potassium iodide by means of free nitrous acid, nitric oxide is formed, but that if dissolved oxygen is present, the latter combines with the nitric oxide, forming NO_2 or N_2O_3, which in presence of acid liberates a fresh quantity of iodine.

Note by Abstractor.—The method is almost exactly identical with that described by Thresh (Trans., 1890, 185), with the modification that instead of carrying out the titration in a current of coal gas, the liquid to be tested is covered with a layer of petroleum.
　　　　　　　　　　　　　　　　　　　　H. G. C.

Estimation of Nitrogen in Coal Gas. By L. LANG (*Chem. Centr.*, 1893, ii, 773; from *J. f. Gasbel.*, 493—494).—20 c.c. of the sample of gas is measured in the Bunte's burette, mixed with 125 c.c. of air, and exploded in a Hempel's pipette. Carbonic anhydride and oxygen are now absorbed as usual, and the remaining nitrogen is measured. Any excess over the amount of nitrogen present in the air is supposed to have been present in the gas.　　　L. DE K.

Adulteration of Basic Slag. By E. WRAMPELMEYER (*Landw. Versuchs-Stat.*, **43**, 183—190).—Natural phosphorite is sometimes coloured so as to resemble basic slag; finely powdered coal is sometimes added for this purpose. The following methods for detecting adulteration are given:—(1) Estimation of loss on ignition in a Rössler furnace. The loss in old samples of basic slag is slight, whilst with fresh samples there is a gain owing to oxidation. (2) Estimation of substance soluble in warm water after ignition. (3) Determination of sp. gr. Basic slag has a sp. gr. = 1·9 or higher, whilst all the other phosphates examined varied from 1·1 to 1·6. (5) Estimation of phosphoric acid soluble in citric acid (Loges' method) and in ammonium citrate (Petermann's method). Results of examination of various phosphates show that the microscopic examination and sp. gr. alone are generally sufficient for ascertaining whether the slag is genuine or not. In two cases, however, the microscopic examination, solubility in water, citric acid, and ammonium citrate indicated genuine slag, whilst the low sp. gr. and the high loss on ignition clearly pointed to adulteration.

The suspected sample should always first be examined with a microscope, then, if necessary, the loss on ignition and sp. gr. and solubility in water determined, lastly, if any doubt remains, the solubility determined by Loges' and Petermann's methods.

<div align="right">N. H. M.</div>

Estimation of Carbon in Steel. By R. LORENZ (*Zeit. angw. Chem.*, 1893, 635—637).—The author, in reply to de Koninck, states that fusion with lead chromate in a current of oxygen at a white heat (Abstr., 1893, ii, 491) causes the complete oxidation of the carbon, and doubts whether the same satisfactory result could be obtained by the use of borax or microcosmic salt, even when mixed with copper oxide.

<div align="right">L. DE K.</div>

Volumetric Estimation of Silver. By G. DENIGÈS (*Compt. rend.*, **117**, 1078—1081).—The reaction between silver nitrate and potassium cyanide, with formation of silver potassium cyanide, proceeds regularly in presence of ammonia, and the end reaction is made very sensitive by adding a small quantity of potassium iodide to the liquid. The result is not affected by considerable variations in the proportion of ammonia, or by the presence of alkali hydroxides, carbonates, chlorides, bromides, phosphates, &c. It is, therefore, not only a very accurate process for the estimation of hydrocyanic acid or cyanides, but, by using a standard solution of potassium cyanide, it can be employed for the estimation of any silver compound whatever.

A solution of about 10 grams of potassium cyanide per litre is used, and will remain unchanged for many days, its stability, especially in hot solutions, being increased by the presence of excess of alkali.

The quantity of substance taken for analysis should contain about one-thousandth of a gram equivalent of silver, and is dissolved in 10 c.c. of ammonia solution and 5 c.c. of water, with the aid of heat if necessary. The ferrocyanide, bromide, and iodide will not dissolve until the standard cyanide solution is added. The phosphate, arsen-

ate, chromate, oxide, and sulphide should be dissolved in nitric acid and then mixed with excess of ammonia. In all cases the liquid containing a slight excess of ammonia is mixed with 20 c.c. of standard cyanide solution, about 100 c.c. of water, and a small quantity of potassium iodide solution, and decinormal silver nitrate solution is added gradually with constant agitation until a slight, permanent turbidity is produced. The difference between the volume of silver solution required and that required for the 20 c.c. of standard cyanide solution alone, gives the quantity of silver present in the substance.

This process is available for the volumetric estimation of precipitates of silver chloride ; the direct estimation of chlorides in liquids of animal origin ; the determination of the xantho-uric compounds in urine by precipitation with ammoniacal silver nitrate solution, and estimation of the excess of silver in the filtered liquid ; estimation of potassium iodide by precipitation with ammoniacal silver nitrate solution; and estimation of all substances such as acetylenes, arsenic hydride, antimony hydride, aldehydes, carbonic oxide, &c., which are capable of altering the strength of alcoholic, ammoniacal, or acid solutions of silver salts.   C. H. B.

Electrolytic Analyses. By F. Rüdorff (*Zeit. angw. Chem.*, 450 —453).—The author, in reply to Classen, objects to the processes given in that chemist's work, and thinks his own methods are more accurate (compare Abstr., 1893, ii, 93—95).   L. DE K.

Volumetric Estimation of Copper with Sodium Sulphide. By A. Bornträger (*Zeit. angw. Chem.*, 1893, 517—524).—The author prepares the sodium sulphide solution by dissolving 40 grams of the commercial sulphide in 1 litre of water. This solution is standardised by means of a solution containing 69·278 grams of crystallised copper sulphate per litre. 10 c.c. of the solution is mixed with a little ammonia, and titrated in the cold with the alkaline sulphide until a drop of the supernatant liquid gives no coloration with acetic acid and potassium ferrocyanide. The process may be used in presence of zinc. The copper solution is rendered alkaline with ammonia, and any iron oxide is filtered off. The addition of the sulphide may at first also precipitate a little of the zinc, but this rapidly redissolves as long as a trace of copper is present. The process may be recommended for the assay of brass, commercial copper sulphate, and a variety of copper sulphate disinfectants.   L. DE K.

Separation of Lead from Copper by Electrolysis. By H. Nissenson (*Zeit. angw. Chem.*, 1893, 646).—The author states that Rüdorff is wrong in supposing that the electrolytic separation of copper from lead is only successful when the lead is present in minute quantity, and proceeds as follows :—1 gram of copper ore is dissolved in 30 c.c. of nitric acid of 1·4 sp. gr., diluted to 180 c.c. and electrolysed carefully according to Classen's directions. An accurate estimation of the copper is obtained, even in the case of ores containing 12 per cent. of lead to 20 per cent. of copper.   L. DE K.

Electrolytic Separation of Metals of the Second Group. By S. C. SCHMUCKER (*Zeit. anorg. Chem.*, **5**, 199—210).—The author adds to the solution an excess of bromine to ensure the highest degree of oxidation; tartaric acid is next added, and then an excess of ammonia. The solution, after being put into a platinum dish, is now electrolysed as usual, the strength and duration of the current varying somewhat according to the nature of the metallic salts. For instance, in the separation of copper from tin, the solution containing about 0·1 gram of each metal in 175 c.c. of liquid was exposed to the galvanic action for 17 hours, the current yielding 0·4 c.c. of electrolytic gas per minute. The copper was completely recovered, and perfectly pure.

The tartaric acid method has proved successful in the separation of copper from arsenic, antimony, and tin; cadmium from antimony; cadmium from tin; cadmium from arsenic; cadmium from arsenic, antimony, and tin; bismuth from arsenic; bismuth from antimony; bismuth from tin; bismuth from arsenic, antimony, and tin; mercury from tin; mercury from arsenic; mercury from antimony; mercury from arsenic, antimony, and tin. The author has not, as yet, tried any experiments with lead when mixed with tin, arsenic, or antimony.

L. DE K.

Estimation of Manganese Oxides by means of Hydrogen Peroxide. By H. C. JONES (*Compt. rend.*, **117**, 781—783).—The method described by Carnot (Abstr., 1893, ii, 427) is only a special case of the general method described by the author (*Amer. Chem. J.*, **12**, 275), which is applicable also to the higher oxides of lead.

C. H. B.

Detection of Nitronaphthalene in Mineral Oils. By N. LEONARD (*Chem. News*, **68**, 297).—α-Nitronaphthalene is added to mineral oils to remove the fluorescence, and may be detected by gently warming and agitating the oil with zinc dust and hydrochloric acid; the characteristic odour of α-naphthylamine will indicate the previous existence of the nitro-derivative; this may be confirmed by the blue precipitate, quickly changing to purple, obtained when ferric chloride is added to a portion of the acid aqueous solution of the amine previously neutralised with ammonia; also by the production of a yellow colour, changing to crimson with hydrochloric acid, when another portion of this liquid is rendered alkaline with soda, extracted with ether, the ether evaporated from the extract, and the residue dissolved in a small quantity of alcohol and treated with a drop of a solution of sodium nitrite and acidified with acetic acid.

D. A. L.

Estimation of Cresol or Xylenol. By F. KEPPLER (*Chem. Centr.*, 1893, ii, 892—893; from *Arch. Hygiene*, **18**, 51—66).—A mixture of potassium bromide and bromate is added to the solution containing the cresol. After adding a sufficiency of sulphuric acid, the liquid is filtered through glass wool, and an aliquot part of the filtrate is titrated, as usual, by means of potassium iodide and sodium thiosulphate with starch as indicator.

L. DE K.

Checking Fehling's Solution. By A. BORNTRÄGER (*Zeit. angw. Chem.*, 1893, 600—601).—The author has come to the conclusion that the standard solution of invert sugar used to check the Fehling solution should be prepared at the ordinary temperature. Pure saccharose is easily prepared by precipitating a filtered, concentrated solution of sugar candy with alcohol and drying the precipitate. 19 grams of this product is dissolved in dilute hydrochloric acid containing 4·5 per cent. of HCl in a 100 c.c. flask. After standing over night, 25 c.c. is pipetted off, coloured with a little litmus, exactly neutralised with alkali, and made up to 1 litre. This solution contains 0·5 per cent of invert sugar.   L. DE K.

Sugar in the Blood. By F. SCHENCK (*Pflüger's Archiv*, **55**, 203—211).—The following method of estimating sugar in the blood is recommended : 50 c.c. of blood is mixed with 50 c.c. of water ; to this, 100 c.c. of 2 per cent. hydrochloric acid and then 100 c.c. of 5 per cent. mercuric chloride are added. The mixture is filtered, and the filtrate decomposed with hydrogen sulphide. This is again filtered, 150 c.c. of the filtrate taken, and air passed through it to get rid of the hydrogen sulphide : it is concentrated to 100 c.c., and then titration is performed by Knapp's method. The mercuric chloride appears to give as good results as the more expensive iodide.

When the blood coagulates, the disappearance of sugar is very great ; it may be 25 per cent. If kept uncoagulated by an oxalate, the loss is insignificant. If blood is acidified, the loss is practically *nil*.   W. D. H

Use of Methylene-blue for the Detection and Estimation of Sugar in Urine. By N. WENDER (*Chem. Centr.*, 1893, ii, 670—671 ; from *Pharm. Post.*, **26**, 393—397).—Ihl observed that methylene-blue is decolorised, by reduction to the leuco-compound, by invert sugar, dextrose, dextrin, &c., whilst it is not acted on by cane sugar. Urea, uric acid, and the inorganic salts in urine are without action on methylene-blue ; creatinine decolorises it with tolerable rapidity ; creatine, after boiling for some time, and albumin, when it is present to the extent of some tenths of a per cent. Animal gum and glycuronic acid may also decolorise methylene-blue ; concentrated alkalis decolorise it rapidly with separation of the free base, but dilute alkalis do not produce any effect. All normal urines in the undiluted state decolorise alkaline methylene-blue solutions on heating ; 1 c.c. normal undiluted urine decolorises 1 c.c. of methylene-blue solution (1 : 1000). To decolorise the same amount of methylene-blue, about 4·5 c.c. of 10 times diluted normal urine is required, whilst only 1 c.c. of a similarly diluted diabetic urine, containing 0·5 per cent. of sugar, produces the same effect. In order to detect the presence of sugar in urine, the following method is adopted : 5 or 10 c.c. of the urine is diluted to 10 times its volume ; 1 c.c. of this solution is then treated with 1 c.c. of aqueous methylene-blue solution (1 : 1000) and 1 c.c. of normal potash, diluted with about 2 c.c. of water, and boiled over a naked flame for a minute. In the presence of 0·5 per cent. of sugar, total decolorisation takes place. If the coloration remains, the urine may be considered as not diabetic.

Quantitative experiments showed that 1 mol. of methylene-blue is reduced by 1 mol. of dextrose. 1 c.c. of methylene-blue solution, $1:1000 = 0.001$ gram methylene-blue would be reduced by 0.005 gram of dextrose. The decolorising power of a normal urine, therefore, corresponds with that of a 0.11 per cent. solution of dextrose. If p is the percentage of sugar in the urine which has to be determined, v the dilution factor, c the number of c.c. of the methylene-blue solution required, then $p = 0.05 \ v/c$.

The determination of sugar in urine is carried out in the following manner. If sugar is found by the qualitative test, the urine is diluted according to its specific gravity.

Sp. gr.	$1.017 - 1.025$	$1.025 - 1.030$	$1.030 - 1.038$
	(50 times)	(100 times)	(200 times)

The volume of the diluted urine which is required to exactly decolorise 0.001 gram of methylene-blue is then determined, several titrations being made. 1 c.c. of methylene-blue solution and 1 c.c. of normal potash are put into a test tube, and the urine run in gradually from a burette, the liquid being boiled once or twice. This process is repeated until the exact amount of urine required has been found. The results obtained by the author fall between those given by the polarisation method and by the reduction of Fehling's solution. Owing to the great dilution of the urine, the disturbing influence of the other constituents of urine which are capable of reducing methylene-blue is scarcely perceptible. A. H.

Estimation of Saccharose in Mixtures of Maltose, Isomaltose, Dextrin, and in Worts. By J. JAIS (*Chem. Centr.*, 1893, ii, 893—894; *Zeit. ges. Brauw.*, 16, 349—351).—The author has carefully investigated Meissl's inversion method, and has found that it is perfectly trustworthy. L. DE K.

Glycogen. By S. FRÄNKEL (*Pflüger's Archiv*, 55, 378—379) and J. WEIDENBAUM (*ibid.*, 380—391; compare Abstr., 1893, i, 186).—In reply to Weidenbaum's criticisms on the trichloracetic acid method of estimating glycogen, the author reaffirms his position, and charges his critic with error, suggesting that he used impure preparations of trichloracetic acid.

To this, Weidenbaum replies by publishing analyses of his trichloracetic acid and a number of fresh experiments in which his former conclusions that Fränkel's glycogen contains nitrogen, and that the glycogen is only imperfectly extracted from the tissues by the use of the acid, is fully confirmed. W. D. H.

Glycogen. By W. GULEWITSCH (*Pflüger's Archiv*, 55, 392—393) and by C. PFLÜGER (*ibid.*, 394—401; compare Abstr., 1993, ii, 601). —Gulewitsch points out that Pflüger was not the first to suggest a method for overcoming the difficulties often experienced in the use of Brücke's reagent for the estimation of glycogen. This and certain small points of detail in the methods suggested furnish matter for the polemical portions of the two papers here under review. W. D. H.

Estimation of the Acidity of Vinegar. By L. VANINO (*Zeit. angw. Chem.*, 1893, 676—677).—The author strongly recommends the process originally worked out by Baumann and Kux. 10 grams of the sample of vinegar is mixed with a solution of 4 grams of potassium iodide and 0·8 gram of potassium iodate and introduced by means of a pipette into the bottom part of an ordinary specimen tube, inside which is sealed a small glass cylinder, which contains the alkaline solution of hydrogen peroxide. After standing for at least two hours, the glass is connected with the author's apparatus (Abstr., 1891, 615), which is easier to manipulate than Wagner's azotometer used in Kux's experiments. The two solutions are mixed and the liberated oxygen is finally read off with the usual precautions. The acetic acid is calculated from the volume of gas at N.T.P., or Kux's tables may be used.   L. DE K.

Estimation of Malic acid. By C. MICKO (*Chem. News*, 68, 286).—To facilitate the separation of malic acid in wines by means of lead acetate, the author evaporates 100 c.c. of wine, or 50 c.c. of cider, to a few c.c., sets aside for an hour with 4 or 5 c.c. of binormal sulphuric acid, then, while agitating continuously, gradually mixes in 50 c.c. of strong alcohol and 50 c.c. of ether. After 6 to 10 hours, filtering and washing with ether-alcohol ensue, and the ether and alcohol are subsequently expelled by distillation over a water bath, but finishing off in a vacuum. Chlorides are removed from the residue by cooling it to 50° or 60° and adding the smallest possible excess of freshly prepared silver sulphate and filtering. The filtrate is neutralised with potassium carbonate, evaporated to a small volume, and is ready to be further treated for the separation of malic acid.   D. A. L.

Butter Testing. By E. SPAETH (*Zeit. angw. Chem.*, 1893, 513—515).—The author uses a kind of weighing flask, the lid and bottom of which are trebly perforated. The bottom, inside, is covered with asbestos. A glass boat, filled one-third with pieces of pumice the size of a pea, is introduced, and the whole is dried for an hour at 105°. The boat is taken out and placed on the balance pan alongside the weighing flask, and weighed. An average lot of butter, weighing about 10 grams, is now put into the boat, and the whole is again weighed. The boat is now placed first on an open water bath for half an hour, then inside an air bath for about two hours at 100°. After cooling, it is put inside the weighing bottle, the whole is re-weighed, and the loss represents the water.

The fat is estimated by placing the whole apparatus inside a Soxhlet tube, and extracting the fat with ether in the usual manner. The salt may be estimated by digesting the insoluble residue in water and estimating the chlorine with silver nitrate. The test analyses show the process to be handy and accurate.   L. DE K.

Butter Analysis. By C. VIOLLETTE (*Compt. rend.*, 117, 856—858).—The weight in a vacuum of 1 c.c. of butter at 100° varies from 0·86320 to 0·86425 gram, whilst for margarine the corresponding values are 0·85766—0·85865 gram. The density of a mixture of butter

and margarine is exactly the mean of the densities of its constituents. When cows are fed chiefly on hay, the density of the butter is about 0·86320, whilst if the food consists of grains, pulp, cake, and meal, with very little hay, the density of the butter is about 0 86425. Out of 150 samples of butter, two only, derived from cows highly fed with grains, meal, and cake, gave densities as high as 0·86530 and 0·86540 respectively, whilst one, derived from a cow fed on straw and hay, had a density of 0 86277.

The author has therefore constructed a densimeter, giving all the densities at 100° comprised between those of pure butter on the one hand and margarine on the other, each unit in the fourth decimal place corresponding to a length of 1·4 mm. on the scale. The butter to be examined is heated in a cylindrical copper vessel by means of steam.

For practical purposes, a series of smaller densimeters is used, which allow first of an approximate, and, afterwards, of a more accurate, classification of the butters under examination. Experiments must be made from time to time with average butters from the same district, and from animals fed on various diets. In doubtful cases the butter must be analysed. C. H. B.

Analysis of Lard. By C. A. NEUFELD (*Chem. Centr.*, 1893, ii, 778; from *Arch. Hygiene,* **17**).—The author comes to the conclusion that neither Hübl's test, nor the silver reaction, are of much use in testing for small quantities of adulterants. L. DE K.

Estimation of Beef Fat in Lard. By W. F. K. STOCK (*Analyst,* **19**, 2—7).—The author's process is based on the slight solubility of beef stearin in ether at 13°. The requisites are : six 25 c.c. graduated test-mixers fitted with glass stoppers ; ether of 0·720 specific gravity ; a set of mixtures of pure lard melting at 34—35° with 5, 10, 15, and 20 per cent. of beef stearin melting at 56° ; a second set of mixtures of pure lard melting at 39—40° with beef fat melting at 50°.

The melting point of the sample is taken by the capillary tube method 24 hours after the tube has been filled. Suppose the melting point to be at 34°, 3 c.c. of the melted fat is run into one of the test-mixers and dissolved in 21 c.c. of ether, then placed in water at 20—25°. 3 c.c. of each of the first set of mixtures is dissolved in exactly the same way. The five tubes are then cooled down to 13° and allowed to remain at that temperature (particularly towards the last) for 24 hours. The apparent volume of deposit in each tube is then noted, and this will give an immediate clue as to the condition of the sample. The ether is poured off from the tubes as far as possible, and 10 c.c. of fresh ether at 13° is added in each case. The stoppers are inserted, the tubes well shaken, and after the deposit has settled the operation is repeated. The whole contents of the tubes are now transferred to weighed shallow beakers. The ether is carefully run off, and the deposits are dried for 15 minutes at 10° The beakers are cooled and weighed and the standard weight nearest to that of the sample is used as the factor by which to calculate the beef fat. For samples with a higher melting point, the second set of

mixtures should be used. The actual presence of beef fat must be proved by the microscope. For this purpose, a few particles of the dry residue are placed on a slide, moistened with alcohol, and covered. Very moderate pressure should be applied to the cover, and the slide viewed with a 1-inch objective and the C eye-piece. The presence of beef stearin may often be recognised by the naked eye.

As regards pure lard, the author is enabled to state that no sample melting below 39° gives more than 0·011 gram of ether-washed deposit. A sample melting at 45·8° gave, however, 0·146 gram of deposit. This shows the necessity of having the two sets of standard mixtures and carrying out the analysis by a strict comparison test. Direct experiment has shown that neither cotton oil, palm-nut-kernel oil, nor cocoa-nut oil, interferes with the deposition of the crystals of beef stearin.   L. DE K.

Furfuraldehyde as a Test for Sesame Oil. By V. VILLAVECCHIA and G. FABRIS (*Zeit. angw. Chem.*, 1893, 505—506).—The authors recommend the following method for the detection of sesame oil. 0·1 c.c. of a 2 per cent. alcoholic solution of furfuraldehyde is put into a test glass and mixed with 10 c.c. of the sample of oil and 10 c.c. of hydrochloric acid (sp. gr. 1·19). After shaking for half a minute, the mixture is left to itself. If less than 1 per cent. of sesame oil is present, the acid liquid will become carmine-red. In the absence of sesame oil the acid layer will be either colourless or of a dirty-yellow colour. The test may also be carried out as follows :— 0·1 c.c. of the furfuraldehyde solution is put into a test glass, mixed with 10 c.c. of oil and 1 c.c. of hydrochloric acid. After thorough shaking, 10 c.c. of chloroform is added to dissolve the oil. In presence of sesame oil, the acid layer will present a fine carmine-red colour, and in its absence there will be either no colour at all or only a trace of green.

By saponifying sesame oil with barium hydroxide and treating the alcoholic extract of the soap with light petroleum, the authors have succeeded in isolating the chromogenic principle.   L. DE K.

Estimation of Alkaloïds by Hulsebosch's Process. By F. LIEUNIGH (*Chem. Centr.*, 1893, ii, 890—891; from *Pharm. Centr. Halle*, **34**, 591—593).—The author rejects the process as being utterly untrustworthy, but suggests a few possible improvements in the apparatus, and also recommends liberating the alkaloïds by means of lime instead of by sodium hydroxide.   L. DE K.

Detection of Piperazine in Urine. By BIESENTHAL (*Chem. Centr.*, 1893, ii, 624—625; from *Therap. Monatsh.*, 1893, 356).— Rörig found (*Therap. Monatsh.*, 1893, 117) that in two cases the addition of picric acid to the urine, after administering piperazine, produced precipitates, which he regarded as albumin. The author considers that these were due to piperazine itself, since this substance, even when diluted 1 : 20,000 with water, gives a distinct precipitate with picric acid and passes through the organism without change. Usually piperazine shows itself in the urine 3—4 hours after having

been taken; the precipitate produced in such urine with picric acid has the characteristic crystalline form of piperazine picrate, and cannot be mistaken for albumin picrate. The piperazine urine gives none of the reactions of albumin. The identity of the precipitate with piperazine picrate was further shown by decomposing it with hydrochloric acid, removing the picric acid by agitation with ether, and detecting the piperazine by means of a solution of potassium bismuth iodide. The presence of piperazine could even be detected in the urine itself by the use of this reagent. In order to detect albumin along with piperazine in urine, acetic acid may be employed; this coagulates the albumin on heating, and the coagulum does not redissolve, whereas the precipitate of piperazine picrate disappears on heating and reappears on cooling. A. H.

Test for Cocaïne. By SCHAERGES (*Chem. Centr.*, 1893, ii, 888; from *Schweiz. Woch. Pharm.*, **31**, 341—343).—A few centigrams of the alkaloïd is dissolved in a drop of water and a drop of sulphuric acid. On adding to the colourless solution a drop of a solution of potassium chromate, or dichromate, a rapidly-vanishing precipitate is obtained. On warming, the liquid turns green and gives fumes resembling those of benzoic acid. Cocaïne is distinguished from morphine by its insolubility in cold solutions of fixed alkalis.

L. DE K.

Detection of "Saccharin" in Wines and Beers. By E. SPAETH (*Zeit. angw. Chem*, 1893, 579—581).—To detect saccharin in wines or cordials, the sample is mixed with purified sand, evaporated to about 10—20 c.c., acidified with a few c.c. of phosphoric acid, and extracted, at a gentle heat, with a mixture of equal parts of ether and light petroleum (b. p. 60°). After filtering through asbestos, the mass is again extracted until the filtrate measures about 200—250 c.c. After distilling off the solvent, the residue is taken up with a very weak solution of sodium carbonate and tasted. A sweet taste points to the presence of "saccharin," the amount of which may be ascertained as usual by a fusion with nitre and an estimation of the sulphate so produced.

When applying the process to beers, the bitter principles of the hops must be first removed by adding a few crystals of copper nitrate. The liquid need not be filtered. L. DE K.

Reaction of Indoles. By A. ANGELI (*Gazzetta*, **23**, ii, 102—103). —On melting a trace of an indole or indolecarboxylic acid with dehydrated oxalic acid in a test tube, a beautiful coloration is produced, and can be dissolved in acetic acid. Indole and its aliphatic derivatives give a magenta colour, whilst α-phenylindole yields a violet colouring matter. W. J. P.

Process for the Full Analysis of Root Crops. By A. v. ASBÓTH (*Chem. Zeit.*, **17**, 725—726).—The author recommends the following process for the analysis of potatoes:—The substance is cut into thin slices, and about 8 grams of the sample is dried, first at 50°, and then at 110°. The loss represents the moisture. If the

temperature is raised too rapidly, the starch gelatinises, and is then very difficult to dry. The dried substance is incinerated, and the mineral matter weighed. For the estimation of the other constituents, about five potatoes are cut up, partially dried at 50°, reduced to powder, and then finely ground; the flour is then subjected to analysis. The remaining moisture is determined by drying at 110°, and the total nitrogen is determined by Kjehldahl's process as modified by the author. [The substance is boiled with sulphuric acid and copper sulphate, potassium permanganate being only used in extreme cases; the liquid is distilled with aqueous soda containing Rochelle salt, and the ammonia is then titrated.—ABSTRACTOR.] The fatty matter is estimated by exhausting 10 grams of the flour with ether in a Soxhlet's tube, the residue being exposed to the air until all the ether has gone off. About 2 grams of it is taken for the estimation of the starch and dextrin by the author's baryta method (Abstr., 1887, 868), but it is necessary to redetermine the moisture and make due correction for any alteration. The minor constituents are estimated by triturating 5 grams of the flour with cold water, and collecting the insoluble mass on a weighed filter. After drying, a portion of it is used for a nitrogen estimation (insoluble proteïds). The solution is evaporated on the water bath, and the residue finally dried for three hours over sulphuric acid in a vacuum; this gives the total soluble matter; it is then treated with water, and any proteïd matter which has coagulated is collected on a weighed filter, dried, and weighed.

The filtrate is concentrated to a syrup and mixed with twice its volume of alcohol. The precipitate is washed with alcohol, dissolved in water, and titrated by means of baryta, which gives the dextrin. The alcoholic solution is evaporated in a platinum dish, and the residue, after drying in a vacuum, is weighed; this gives the sugar and amido-acids. The sugar may be estimated by Fehling's solution, and the amido-acids are then taken by difference; they may, however, also be estimated directly by deducting from the total nitrogen the nitrogen due to the proteïds, and calculating the difference to asparagine, which contains 21·97 per cent. of nitrogen. By taking the sum of the soluble proteïd, dextrin, and asparagine, and deducting this from the matter soluble in water, the difference gives the colouring matters and gummy substances.

In conclusion, the author gives the details of an analysis of a variety of red potato, popularly known as the Zulu-King. Not a trace of sugar was found. As the result is very favourable, the cultivation of this crop on the large scale is much to be recommended.   L. DE K.

The Ferrocyanide Test for Urine. By J. P. KARPLUS (*Chem. Centr.*, 1893, ii, 496; from *Centr. klin. Med.*, **14**, 577).—See this vol., ii, 107.

Estimation of Proteïds and Extractives in Cow's and Human Milk. By I. MUNK (*Virchow's Archiv*, **134**, 519—540).—See this vol., ii, 106.

General and Physical Chemistry.

Absorption Spectra of Solutions of the Chromoxalates of the Blue Series. By G. MAGNANINI and T. BENTIVOGLIO (*Gazzetta*, **23**, ii, 444—451; compare Lapraik, Abstr., 1893, ii, 313). —Ostwald (Abstr., 1892, 1137), from a study of a number of salts, concluded that the similar absorption possessed by very dilute solutions of salts containing one coloured ion in common is due to the complete electrolytic dissociation of the salts, the coefficient of absorption being proportional to the number of coloured ions in solution. Ostwald examined very dilute solutions of the chromoxalates, amongst others, and found their absorption coefficients to be proportional merely to the concentrations.

The authors have measured the absorption of solutions of the chromoxalates of potassium, sodium, and ammonium, and confirm Ostwald's results. They find further, however, that the absorption coefficients are also proportional to the concentration in very concentrated solutions (20—25 per cent.), in which the dissociation is small. The absorption in concentrated solutions thus follows the same law as that in dilute highly dissociated solutions. The absorption coefficient is not altered by the addition of a salt containing the same metallic ion as the chromoxalate, although the dissociation of the latter is so greatly reduced by the over-pressure of the metallic ion. The authors conclude that the absorption of the chromoxalates is absolutely independent of the extent of their electrolytic dissociation.

W. J. P.

Comparative Experiments on the E.M.F. of the Clark Standard Cell. By K. KAHLE (*Ann. Phys. Chem.*, [2], **51**, 174—202).—The experiments detailed in this paper were made with the object of ascertaining the effects which change of form, purity of material, age, and temperature have on the E.M.F. of the Clark standard cell. The H-form devised by Lord Rayleigh, the form proposed by Feussner, and that adopted by the Board of Trade were compared with one another. The results show that the H-cell is far superior to the other two, both in the ease with which it can at any time be reproduced of constant E.M.F. and in the fact that impurities and disturbing influences have less effect on its constancy, so that the variation of its E.M.F. from the normal value can with little difficulty be reduced to 0·0001 volt. Greater changes than this were not observed in cells which were often compared with one another during the course of $1\frac{1}{2}$ years. In the effect which temperature has on this cell, it is also to be placed before the others. The author finds that a knowledge of the temperature coefficients of the Feussner and Board of Trade cells is misleading, as the E.M.F. calculated by their means does not agree with that actually observed. On the other hand, as long as sudden changes of temperature are avoided, the value of the E.M.F. for the H-cell can be calculated for different

temperatures to within 0·0001 volt, and even with sudden tempera-
ture changes to within 0·001 volt. The coefficient for temperatures
between 10° and 30° was found to be $-0·000814 -0·000007 (t-15)$.

The constancy discovered in the E.M.F. of the above form of the
Clark standard cell leads the author to propose its adoption for the
purpose of defining the unit of electromotive force. He condemns
the form of cell adopted by the Board of Trade as not sufficiently
fulfilling the requirements of a standard.   H. C.

**Instructions for the Preparation of the Clark Standard
Cell.** By K. KAHLE (*Ann. Phys. Chem.*, [2], **51**, 203—211).—In-
structions are given for the preparation of the Clark standard cell in
the ├─-form, which the author finds to be the most suitable (see pre-
ceding abstract). The principal points requiring attention are that
the mercury serving as the positive electrode should be as free as
possible from impurity, that the whole of the active surface of the
electrodes should be kept in contact with a solution of zinc sulph-
ate, that is maintained always in a concentrated condition by the
presence of zinc sulphate crystals, and that the zinc sulphate should
contain no free acid.   H. C.

**Electrical Conductivity of some Solutions of Salts, espe-
cially of Calcium, Strontium, and Barium.** By A. C. MAC
GREGORY (*Ann. Phys. Chem.*, [2], **51**, 126—139).—The author has de-
termined the conductivities of solutions of calcium chloride, nitrate,
sulphate, and acetate; strontium chloride, nitrate, and acetate;
barium and silver acetates; and potassium oxalate. The results are
given in tabular and curve form. The curves for the molecular con-
ductivities are in general of a perfectly regular character, and show
little tendency, even with the most dilute solutions, to a departure
from their usually rectilineal character. Silver acetate shows, how-
ever, a change in curvature in dilute solutions, for which no cause
can as yet be assigned.   H. C.

**Electrical Conductivity of Solutions of Salts of Organic
Acids in presence of Boric Acid.** By G. MAGNANINI and T.
BENTIVOGLIO (*Gazzetta*, **23**, ii, 451—457).—The present paper deals
with the influence of boric acid on the electrical conductivity of solu-
tions of salts of various organic acids, the object being to determine
whether Magnanini's method (Abstr., 1893, ii, 506) for detecting
hydroxyl in organic acids could be applied to solutions of the salts.
The behaviour of solutions of sodium acetate, citrate, and salicylate,
potassium and sodium tartrates, and calcium lactate was examined.
The conclusion is deduced that the results obtained with solutions
of the salts are not so certain as with those of the acids.
                                                            W. J. P.

**Densities of Saturated Vapours and their Relation to the
Laws of Solidification and Vaporisation of Solvents.** By
F. M. RAOULT (*Compt. rend.*, **117**, 833—837).—The author, in con-
junction with Recoura, has shown that if d' is the density of a satu-

rated vapour determined experimentally, and d is its theoretical value,

$$\frac{d'}{d} = \frac{f - f'}{f} \frac{100}{P} \frac{M_1}{M},$$

where f and f' are the vapour pressures of the solvent and the solution, P the weight of substance dissolved in 100 grams of solvent, and M and M_1 the molecular weights of solvent and dissolved substance. Since Guldberg has shown that there is a relationship between the depression of the freezing point and that of the vapour tension, the above relation may, in accordance with well-known principles, be transformed into

$$\frac{d'}{d} = 1{\cdot}988 \frac{f - f'}{f\,C} \frac{T^2}{L_1\,M},$$

where C is the reduction of the freezing point, L_1 the latent heat of fusion, and T the absolute temperature. The relationship holds for any dilute solution, and the author shows that it is in general keeping with the theory of dilute solutions, and is verified by experiment.

H. C.

Vapour Tension Measurements. By G. W. A. KAHLBAUM (*Zeit. physikal. Chem.*, **13**, 14—55).— This paper gives the results of a large number of experiments made to test the concordance or disagreement of the statical and dynamical methods of determining vapour pressures. The first liquids employed were water and mercury, in which the author's dynamical measurements agreed well with the statical numbers given by Regnault, by Hertz, and by Ramsay and Young. As Landolt's statical determinations in the case of the first five fatty acids did not agree with the author's previous dynamical determinations, Landolt's work was repeated. Two unavoidable sources of error are considered to affect statical measurement, namely, the impossibility of placing the liquid perfectly free from air in the vacuum chamber of the barometer, and the impossibility of obtaining the liquid absolutely dry ; these the author believes to be the cause of the previously obtained *regular* variation between the results of the two methods. As a result of his determinations, he concludes that the " statical and dynamical methods of vapour tension measurement give concordant results." The differences previously supposed to exist had been regarded as due to the fact that in the statical method it is only the cohesion of the surface molecules which is loosened, whilst in the dynamical method the cohesion of all the molecules, including those in the midst of the liquid, has to be overcome. The author considers, however, that, owing to the presence of air and other particles, surfaces do exist in the midst of the liquid at which evaporation takes place, so that in both methods it is only the cohesion of surface molecules which is concerned. The results of a large number of measurements with different liquids are tabulated, all done by the dynamical method to avoid the abovementioned inevitable causes of error. Tables are given for the vapour pressures at different temperatures, and of the boiling points at different pressures in the case of the first ten normal fatty acids,

for isobutyric, isovaleric, and isocaproic acids, and for mixtures with water and among themselves of some of these liquids. In no case, however, is the pressure higher than 75 mm., the majority of the liquids being observed at pressures varying from 0 to 60 mm. The paper closes with a statement that Dalton's law has as little validity for the homologous fatty acids as for the fatty alcohols, which is contrary to the opinion held by G. C. Schmidt (Abstr., 1891, 969; 1892, 396).   L. M. J.

Dissociation Constants of Water and Hydrocyanic acid. By J. J. VAN LAAR (*Zeit. physikal. Chem.*, **12**, 742—750).—From the experiments of Shields, Bredig, and others the author calculates the following dissociation constants:—

Acetic acid	$k =$	$1800 \cdot 00$	$\times 10^{-8}$
Hydrocyanic acid	$k =$	$3 \cdot 1$	$\times 10^{-8}$
Aniline	$k =$	$1 \cdot 1$	$\times 10^{-8}$
Phenol	$k =$	$0 \cdot 42$	$\times 10^{-8}$
Water	$k =$	$0 \cdot 70$	$\times 10^{-14}$

It will be seen that hydrocyanic acid, which is 600 times weaker than acetic acid, is more than four million times stronger than water.

H. C.

Composition of Saline Solutions deduced from their Indices of Refraction. By P. BARY (*Compt. rend.*, **118**, 71—73).—In a former paper (Abstr., 1892, 929) the author has shown that the presence of hydrates in aqueous solutions may be deduced from the refractive indices of such solutions. The experiments recorded applied only to concentrated solutions, but the method has now been adapted to the examination of solutions of considerable dilution. The refractive indices of dilute solutions of potassium chloride are found to be strictly proportional to the amounts of salt contained in these solutions, and afford no indication of the occurrence of electrolytic dissociation.   H. C.

How the Theory of Solutions Arose. By J. H. VAN'T HOFF (*Ber.*, **27**, 6—19).—In this account of an address delivered to the German Chemical Society, the author first shows how from a consideration of the relations between constitution and chemical properties he was led to consider the rate of chemical actions, the equilibrium of opposed reactions, the thermodynamical basis of the equilibrium, and finally the general problem of affinity. The first affinity problem he investigated was the simple one of the attraction of water by salts with water of crystallisation, and while studying this subject he became acquainted with Pfeffer's osmotic researches. A thermodynamical consideration of the two phenomena jointly led to the conception of osmotic pressure in solutions as the analogue of gaseous pressure in gases, and enabled him to show how substances in dilute solution obeyed laws perfectly analogous to the ordinary gas laws, namely those of Boyle, Charles, and Avogadro.

He next deals with the theory of dilute solutions, and deduces from the osmotic pressure (1) the lowering of the vapour pressure,

(2) the elevation of the boiling point, and (3) the depression of the freezing point.

The third section of his address is occupied with the deviations from the simple laws. First, he discusses abnormally small freezing point depressions, then those that are abnormally large, and shows how the latter are accounted for by Arrhenius' hypothesis of electrolytic dissociation. Lastly, he calculates the amount of ionisation of pure water from experiments on the rate of catalysis of ethylic acetate, the minimum velocity predicted by the dissociation theory being experimentally verified.   J. W.

The Hydrate Theory. By S. U. PICKERING (*Ber.*, **27**, 30—31).—In answer to W. Meyerhoffer (this vol., ii, 9), the author, whilst admitting the obvious identity of freezing point and solubility curves, states that it does not, therefore, follow that changes of curvature in them can be caused by changes in the nature of the crystallising substance only, but they can be caused by changes in the constitution of the liquid also, and the whole gist of the present hydrate theory lies in recognising the existence of such changes.   S. U. P.

Cryoscopic Molecular Weight Determinations in Benzene. By K. AUWERS (*Zeit. physikal. Chem.*, **12**, 689—722).—Certain irregularities which have been noticed in the cryoscopic behaviour of benzene solutions have induced the author to make a large number of different observations with a number of such solutions, chiefly with the view of ascertaining the suitability of benzene as a solvent in molecular weight determinations. Substances containing a hydroxyl group, the behaviour of which in benzene Raoult pronounced irregular, are found to behave in the normal manner provided the solutions taken are sufficiently dilute. The phenols in fairly concentrated solution even show this normal behaviour, but the aliphatic hydroxyl compounds give abnormal depressions in concentrated benzene solutions. This behaviour may in certain cases serve as a guide in establishing the constitution of compounds which are supposed to belong to this class. All acids hitherto examined give, in benzene solutions of medium concentration, a depression corresponding with about double the ordinarily-accepted molecular weight. This behaviour also serves as a most important guide in questions of constitution.   H. C.

Solutions of Sodium Silicates and Influence of Time on their Constitution. By F. KOHLRAUSCH (*Zeit. physikal. Chem.*, **12**, 773—791).—See Abstr., 1893, ii, 166.   H. C.

Action of Hydrogen Chloride on Ethylic Alcohol. By J. C. CAIN (*Zeit. physikal. Chem.*, **12**, 751—761).—The action of hydrogen chloride on ethylic alcohol was studied as a time reaction. The fact that the reaction in question is a reversible one was first established. The influence of temperature is very considerable. There is practically no action at 15°, but as the temperature rises the rate of decomposition rapidly increases. The following table, which applies

to a mixture of 100 equivalents of alcohol with 31·2 equivalents of hydrogen chloride, gives the percentage decomposition of the hydrogen chloride in 27 hours at different temperatures.

Temperature	40°	60°	80°	90°
Per cent. HCl decomposed..	6·77	32·34	71·32	90·64

Excess of alcohol exercises a retarding influence, and the same thing applies, but in smaller degree, to the influence of ethylic chloride. The Guldberg-Waage law applies to the action provided the quantity of alcohol taken is sufficient to dissolve the ethylic chloride formed, and that separation of the solution into two layers does not take place.   H. C.

New Apparatus for Sublimation. By G. ODDO (*Gazzetta*, **23**, ii, 313—314).—The following method gives good results in the purification of substances by sublimation. The substance is placed in a small beaker, which is fitted into a hole in a piece of asbestos card standing on a ring support; a beaker, in which the sublimate collects, is then inverted over this, and a third beaker is placed over the second. The beaker containing the substance is heated by radiation from a second asbestos disc placed below it, to which heat is applied by means of a bunsen burner.   W. J. P.

Condensers. By J. WALTER (*J. pr. Chem.*, [2], **49**, 44—48).—Further improvements in the author's form of condenser (Abstr., 1887, 105) are depicted.   A. G. B.

Critical Studies in Preparation Exercises. By S. P. L. SÖRENSEN (*Zeit. anorg. Chem.*, **5**, 354—373).—Considering that for purposes of preparation exercises, a more critical examination of the modes of preparation of inorganic substances is required than is found in available text books, the author has investigated the methods for preparing pure nickel and cobalt compounds. He describes modified methods, for the details of which the original must be consulted, and gives a critical review of the methods which have been proposed by successive investigators, but omits mention of the method of Mond, Langer and Quincke (Trans., 1890, 750) of obtaining absolutely pure nickel by means of nickel carbonyl which has proved to be so successful.   L. T. T.

Inorganic Chemistry.

Hydrogen Sulphide Apparatus. By F. W. Küster (*J. pr. Chem.*, [2], **48**, 595—598). The bottle A (5 litres) is placed at such a height above the bottle B (3 litres) as will serve to supply the *plus* pressure required in the apparatus, and receives the acid (2 vols. of common hydrochloric acid and 1 vol. of water) which is to evolve

hydrogen sulphide from the large pieces of ferrous sulphide in the bottle C (10 litres). The trap D serves to prevent the regurgitation of the aqueous hydrogen sulphide in E. Inasmuch as the water in this last-mentioned bottle is saturated with the gas at the pressure of the apparatus, it is always in the best possible condition for use
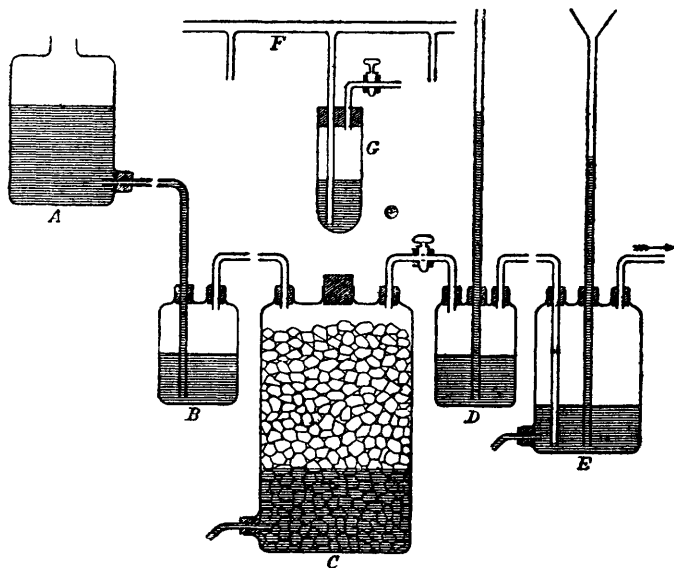
when drawn off by the tap in the bottom of the bottle. The tubes connecting A, B, and C should be drawn out at the ends to allow of only a slow passage of the acid. When the gas is drawn off from the cock of the small washing bottle G, attached to the general supply tube F, the acid falls from A, through B into C, and is driven back when the exit is again closed. Inasmuch as C may be made to hold enough ferrous sulphide to yield 10,000 litres of gas, it is only necessary to see that A is filled with acid, and C emptied of ferrous chloride solution, every morning. A. G. B.

Combination of Hydrogen and Selenium in a Vessel not uniformly heated. By H. PÉLABON (*Compt. rend.*, **118**, 142—144). Ditte has shown that when one part of the extremities of a tube containing selenium and hydrogen is heated above 300°, crystals of selenium appear after a time at another part of the tube, where the temperature is very near the melting point of selenium (about 270°). This particular temperature the author distinguishes as θ. Experiments show that when no part of the tube is at a temperature lower than θ, the final composition of the mixture is that corresponding with the temperature of the coolest part of the tube. In all cases the excess of selenium at the close of the experiment is found at the coldest extremity of the tube.

When the hottest part of the tube is at a temperature higher than, and the coldest part at a temperature lower than θ, the final composition of the mixture is independent of the extreme temperatures of the tube. The excess of selenium condenses at the point where the temperature has the value θ. It would seem that the formation of hydrogen selenide in the hot parts of the tube ought to take place more rapidly than its destruction in the cold parts, and if, in the preceding experiments, the tubes are suddenly cooled before the whole of the selenium has disappeared from the hottest part of the tube, the composition of the gaseous mixture practically corresponds with the highest temperature of the tube.

When no part of the tube is at a temperature as high as θ, the final composition of the gaseous mixture is that which corresponds to the highest temperature of any part of the tube.   C. H. B.

Formation of Hyponitrous acid. By S. TANATAR (*J. Russ. Chem. Soc.*, **25**, 342—345).—When solid hydroxylamine chloride and potassium nitrite are mixed in equivalent proportions, there is a violent action, nitrous oxide being evolved. In dilute solution (1 part NH_3O,HCl to 20 parts water), the reaction takes place, slowly, and in the course of a few hours silver nitrate gives a precipitate of silver chloride, coloured yellow by silver hyponitrite, which may be obtained pure by dissolving it out with nitric acid, and precipitating the solution with sodium acetate. Better results are obtained by adding lime (1 mol.) to the moderately strong solution of potassium nitrite (1 mol.), then the hydroxylamine hydrochloride, heating to 50°, allowing the mixture to remain for a day or two at the ordinary temperature. The filtrate from the excess of lime is acidified with acetic acid, silver nitrate is added, and the hyponitrite separated from the silver chloride as described above. The author recommends this as the best method of obtaining the hyponitrites.   J. W.

The Reaction between Hydroxylamine Hydrochloride and Sodium Nitrite. By S. TANATAR (*Ber.*, **27**, 187; see preceding abstract). The reaction takes place with difficulty in alkaline solution and in the presence of magnesia, zinc oxide, cadmium oxide, and calcium carbonate. If the acid solution of hydroxylamine hydrochloride is first neutralised it does not react with sodium nitrite. The violent reaction between solid hydroxylamine hydrochloride and sodium nitrite does not take place in the presence of lime, magnesia, or zinc oxide.   E. C. R.

Preparation of Phosphorus from the Phosphates of the Alkalis and Alkaline Earths by means of Aluminium: Action of Aluminium on Sulphates and Chlorides. By A. ROSSEL and L. FRANK (*Ber.*, **27**, 52—55).—When sodium metaphosphate is heated with aluminium in a current of hydrogen, 28—31 per cent. of the phosphorus distils over, and a residue is obtained consisting of alumina, sodium aluminate, and aluminium phosphide. All the phosphates of calcium and magnesium, when heated with aluminium,

yield phosphorus. *Aluminium phosphide*, Al_3P_5, is obtained by heating aluminium in phosphorus vapour, and then heating the product until phosphorus ceases to come off. It is a grey, crystalline powder.

The whole of the phosphorus in the phosphates may be obtained by adding silica to the mixture in the proportions represented by the equation $3Ca(PO_3)_2 + 10Al + 3SiO_2 = 3CaSiO_3 + 5Al_2O_3 + 3P_2$.

When a mixture of calcium metaphosphate and calcium sulphate was heated with aluminium, a violent explosion ensued. The authors find that this is due to the sulphate; barium sulphate or calcium sulphate, when heated with aluminium, act with explosive violence, and sulphur is set free. The chlorides are also decomposed by aluminium at a high temperature. E. C. R.

Alkali Orthophosphates. By L. STAUDENMAIER (*Zeit. anorg. Chem.*, **5**, 383—396).—With the intention of determining whether two possible isomeric dipotassium disodium pyrophosphates (one symmetrical, the other unsymmetrical) exist, the author attempted to prepare dipotassium phosphate, K_2HPO_4. Not obtaining satisfactory results, and finding the literature on the subject very conflicting, he has carefully investigated the question. All attempts to prepare dipotassium phosphate proved futile, and the statements of Thomson, Graham, Berzelius, and Mitscherlich, and of chemical text-books in regard to this substance are incorrect.

In the course of experiments to prepare dipotassium phosphate by the action of monopotassium phosphate (KH_2PO_4) on sodium carbonate, rhombic crystals of 1—2 mm. in length were obtained; these are very deliquescent, and exceedingly soluble in water, from which solution, however, the monophosphate crystallises out. The crystals on analysis were found to correspond exactly with the formula $K_5H_4(PO_4)_3,H_2O$. This salt is alkaline in reaction, and on ignition leaves a mixture of potassium pyro- and meta-phosphates. By substituting potassium hydroxide for potassium carbonate, using a rather larger proportion of this, and treating the product in a similar way, the author obtained a salt of the formula $K_7H_5(PO_4)_4,2H_2O$, forming crystals very closely resembling those of the compound just described. It differs from them, however, in that if left on a porous plate exposed to the air, it deliquesces and sinks entirely into the plate, whilst under like conditions the salt $K_5H_4(PO_4)_3,H_2O$ always leaves some monopotassium phosphate on the plate. The author was unable to isolate any potassium salt of a more basic character, even when a much larger proportion of base was used.

The author has also obtained per-acid phosphates of the alkalis. The *potassium* salt, $KH_5(PO_4)_2$, was obtained by mixing, in solution, monopotassium phosphate with phosphoric acid, in molecular proportion, evaporating the solution to a small bulk, and allowing it to remain. It crystallises in long needles, has a very strong acid taste, melts at 127°, and then forms a viscid mass which does not re-solidify. On further heating, water is first evolved, then phosphoric acid, and potassium metaphosphate is left. Alcohol causes the crystals to become opaque, by dissolving the acid and leaving monopotassium phosphate. The

ammonium salt, $(NH_4)H_5(PO_4)_2$, closely resembles the potassium salt in form and properties. The *sodium* salt is isomorphous with the potassium salt, and melts at 131°. L. T. T.

Action of Sodium on Water. By M. ROSENFELD (*J. pr. Chem.*, [2], **48**, 599—601).—The explosion which occurs when water is poured on to sodium has been supposed to be due to the formation of sodium peroxide, which subsequently decomposes, and thus produces an explosive mixture of hydrogen with oxygen. It is now shown that no oxygen can be detected in the gas obtained by passing steam over sodium. The author concludes that the explosion is due to the decomposition of sodium hydride, which may be expected to be formed when sodium acts on water; the conclusion is supported by the observation that the explosion takes place in the centre of the sodium. When steam is passed over sodium no hydride is formed, because the tension of the hydrogen is kept very low by the current of steam. A safe and rapid method for obtaining hydrogen is to pass steam through an iron box, with an air-tight lid, containing sodium. If the passage of steam be continued until no more hydrogen is evolved, and if the quantity of gas be measured, a calculable weight of sodium hydroxide will remain in the box, and will serve for the preparation of a standard solution. A. G. B.

Decomposition of Sodium Dioxide by Aluminium. By A. ROSSEL and L. FRANK (*Ber.*, **27**, 55).—When a mixture of sodium dioxide and aluminium powder is exposed to damp air, spontaneous composition ensues. If the mixture is moistened, a very high temperature is produced. E. C. R.

Hydrates of Lithium Chloride and Bromide. By A. BOGORODSKY (*J. Russ. Chem. Soc.*, **25**, 316—341).—The author describes the preparation and properties of the following hydrates:—
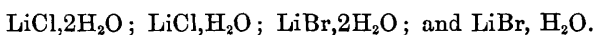
$LiCl,2H_2O$; $LiCl,H_2O$; $LiBr,2H_2O$; and $LiBr, H_2O$.
J. W.

Action of Mercuric Chloride on Metallic Silver. By H. C. JONES (*J. Soc. Chem. Ind.*, **12**, 983—988).—By the action of a solution of mercuric chloride, the metallic silver of a silver photographic image is changed into a white substance hitherto supposed to be a mixture of mercurous and silver chlorides; the author has investigated the matter, and now regards this substance as a compound of the composition $HgAgCl_2$.

Mercuric chloride acts but slowly on silver, and therefore many methods for preparing this substance were tried; finally the following was adopted. A considerable excess of mercuric chloride, made into a thin paste with water, is mixed with pulverulent silver, agitated frequently, and occasionally ground in a mortar, during two or three weeks, then, after heating from 12 to 20 hours in a flask in a water bath, is mixed with a considerable quantity of water in which most of the excess of mercuric chloride is allowed to settle, whilst the turbid supernatant liquid is poured off, and by repeating the operation most of the

preparation is obtained in suspension and soon settles out. The preparation on heating loses mercurous chloride by volatilisation, and silver chloride remains behind; if, however, any free silver be present it is converted into chloride, and a corresponding quantity of mercury volatilises. With excess of mercury, the reverse takes place, inasmuch as it removes some of the chlorine that would otherwise remain as silver chloride.

The sp. gr. of silver chloride is 5·590; of mercurous chloride, 7·258; a difference which would permit of their separation when settling from suspension in water; it has been found, however, that the preparation, when allowed to settle in a long tube filled with water, so as to form a 7-inch layer, shows no signs of separation, material from the top and from the bottom of the layer giving exactly the same numbers on analysis. Moreover, calculation shows that a mixture of equivalent proportions of the two chlorides would have a sp. gr. of 6·626, whereas the sp. gr. of the preparation is 6·505. This substance is slowly affected by light, especially when moist; it also gives the following reactions :—With hydrochloric acid, it yields silver chloride, mercuric chloride, and mercury; with ferrous oxalate, it is completely reduced; with the alkalis, a partial exchange of oxygen for chlorine ensues; with ammonium chloride, potassium chloride, potassium cyanide, or sodium thiosulphate, one-third of both silver and mercury remains as a metallic residue, the rest dissolves; with sodium sulphite, one-half the silver and one-third of the mercury remains undissolved as a metallic residue; with potassium silver cyanide, all the silver is deposited as metal; with ammonia, substituted ammonium salts are obtained containing both silver and mercury. The author considers that he adduces sufficient evidence to support his view that the substance in question is not a mere mixture of mercurous and silver chlorides, but is a compound of the composition $HgAgCl_2$; for, only the first three of the above reactions could be explained on the mixture assumption, whilst all of them can be explained by use of the author's formula. Incidentally it is noted that mercuric chloride has been observed to act on the mixed metallic residues obtained in the above reactions somewhat in this way: $HgAg + 2HgCl_2 = Hg_3AgCl_4$. D. A. L.

Molecular Weight of Mercurous Nitrate determined by the Cryoscopic Method. By F. Canzoneri (*Gazzetta*, **23**, ii, 432—437). —The author has determined the depression of the freezing point of dilute nitric acid by mercurous nitrate, and concludes that the salt has the molecular formula $Hg_2(NO_3)_2$. The freezing points of only two solutions of the salt were determined. W. J. P.

Ceric Dichromate. The Separation of Cerium from Lanthanum and Didymium. By G. Bricout (*Compt. rend.*, **118**, 145—146).—When an electric current of 2·5 to 3 volts. is passed through the slightly acid solution, obtained by dissolving cerous carbonate in chromic acid, a large positive electrode being used, small, brilliant, orange-red crystals of ceric dichromate, $CeO_2,2CrO_3,2H_2O$, separate on the positive electrode. This compound is insoluble in

water, but dissolves in acids. It is slightly decomposed by cold
water, and when boiled with water is first converted into yellow ceric
chromate, and eventually into hydrated ceric oxide.

Lanthanum and didymium form no higher oxides, and hence, under
similar conditions, give no deposit on the positive electrode. Ceric
dichromate, precipitated in the manner described, from solutions con-
taining lanthanum and didymium, is quite free from these elements,
and can readily be dissolved in hydrochloric acid and precipitated in
the form of oxalate.   C. H. B.

Electrolysis of Ferrous Sulphate. By M. TICHVINSKY (*J. Russ.
Chem. Soc.*, **25**, 311—315).—When a 30 per cent. solution of ferrous
sulphate is electrolysed between iron electrodes by a very weak
current in the dark, a solution is obtained in the course of a month
or two which differs considerably from the ordinary solutions of
ferrous salts. Its colour is more intensely green, somewhat like that
of nickel sulphate, and on exposure to light, it deposits a green solid,
which may be preserved for an indefinite period if air is excluded.
Analysis of the solution showed it to contain twice as much iron for a
given quantity of sulphuric acid as is contained in ferrous sulphate.
It therefore probably contains the basic salt $FeSO_4,FeO$, which decom-
poses on exposure to light with deposition of $Fe(OH)_2$, coloured green
by some ferrous sulphate carried down along with it. This appears
likely, because the precipitate on washing becomes much paler.
                                                        J. W.

Action of Ferric Salts on Iodides. By K. SEUBERT (*Zeit. anorg.
Chem.*, **5**, 334—338).—This paper forms a historical introduction to
the paper of Seubert and Dorrer (see next Abstract). The author
points out that this reaction is generally represented by the equation
$Fe_2Cl_6 + 6MI = 2FeI_2 + 6MCl + I_2$, or $Fe_2Cl_6 + 2MI = 2FeCl_2 + 2MCl + I_2$,
but that neither of these represents the true facts. For, whilst in
strong solutions, and with a large excess of iodide, the theoretical
quantity of iodine may be liberated, in general less than this quantity
is set free, the quantity in weak solutions showing a considerable
deficiency. Very weak solutions of ferrous chloride even absorb
iodine with the formation of some ferric salt. It is thus clear that
this reaction is a reversible one.   L. T. T.

**Action of Ferric Chloride on Potassium Iodide and on
Hydriodic acid.** Part I. By K. SEUBERT and A. DORRER (*Zeit.
anorg. Chem.*, **5**, 339—353).—In this part of the paper, the results
of the action of neutral solutions of ferric chloride on potassium
iodide are described. Deci-molecular solutions were used ($FeCl_3$
being considered as the molecule of ferric chloride), and quantities of
of 10 c.c., or multiples thereof, taken so as to correspond, on the one
hand, with 1 to 50 mols. of potassium iodide to 1 mol. of ferric
chloride, and on the other with 1 to 10 mols. of ferric chloride to 1 mol.
of potassium iodide. The influence of time and of dilution on the

reaction was also studied. The results are given in a series of full tables and curves, which may be thus summarised.

1. *Influence of time on the reaction.*—In order to allow the progress of the reaction to be followed, the mixed solutions were, in these series, always diluted to 100 c.c. The progress of the reaction, where the two substances are used in molecular proportion, is most rapid in the first quarter of an hour, by the end of which time about 28 per cent. of the theoretical quantity of iodine has been set free, and then rapidly decreases until after five or six hours (at which time 50–51 per cent. of the theoretical iodine has been liberated), further action is exceedingly slow. At the end of 46 hours, 60 per cent. of the theoretically possible iodine has been set free. The reaction, when the molecular proportions are equal, does not seem to proceed much beyond this point; but when unequal molecular proportions are used, the progress of the reaction is quicker, the end state of equilibrium is sooner reached, and the total quantity of iodine liberated is greater the greater the excess of either reagent employed, excess of potassium iodide exerting, however, a somewhat greater influence than excess of ferric chloride.

2. *Influence of the mass of the two reagents on the reaction.*—As already seen, the total quantity of iodine liberated by the mutual action of potassium iodide and ferric chloride in molecular proportion is below 60 per cent. of that required by the theoretical equation. Increase of either reagent augments this quantity. At first, increase of potassium iodide has more effect than a similar increase of ferric chloride. But, after a time, the effect of increasing the iodide ceases, and about 96–97 per cent. of the theoretical iodine is the most that can be liberated in this way. With excess of ferric chloride, on the other hand, the influence is at first less, but continues more regularly, and when the proportions reach about $20FeCl_3$ to $1KI$, the whole of the theoretically possible iodine is liberated, or, in other words, the reaction is complete.

In the second part of this paper the authors propose to discuss the theory of this reaction. L. T. T.

Atomic Weight of Palladium. By E. H. KEISER and Miss M. B. BREED (*Amer. Chem. J.*, **16**, 20—28).—The authors have prepared palladium diammonium chloride from palladium dichloride purified by distillation in a current of chlorine, and from metallic palladium, which was dissolved in *aqua regia*, the solution freed from acid by evaporation, treated with excess of ammonia, warmed, filtered, and the dichloride precipitated with gaseous hydrogen chloride. Both these methods give a product of undoubted purity, and one in which the ratio of palladium to palladium diammonium chloride is such as is equivalent to an atomic weight of 106·25 for palladium (mean of 10 determinations: $H=1$; $N=14·01$; $Cl=35·37$), a number very closely agreeing with 106·27, that obtained by Keiser in previous determinations (compare Abstr.,1 890, 17). The method employed for converting the double salt into the metal was that of heating it in a current of pure hydrogen, and the experiments were conducted in such a way as to conclusively establish the fact that no loss of palladium occurred

by volatilisation or decrepitation (compare Keller and Smith, Abstr.,
1893, ii, 73).   G. T. M.

Mineralogical Chemistry.

Artificial Trona.   By B. REINITZER (*Zeit. angw. Chem.*, 1893, 573—575).—The author notes an error in a reference to his work by C. Winkler (Abstr., 1893, ii, 577), in that the analyses made by him in 1887 did not lead to the formula for trona then generally accepted, but to the formula $Na_2CO_3 + NaHCO_3 + 2H_2O$. This formula is identical with that given by Winkler.

In a subsequent communication, C. WINKLER (*Zeit. angw. Chem.*, 1893, 599) corrects the error, and explains how it originated.

<div align="right">B. H. B.</div>

Composition of Staurolite.   By S. L. PENFIELD and J. H. PRATT (*Amer. J. Sci.*, **47**, 81—89).—In the early analyses of staurolite, especially in those by Rammelsberg, a great variation was found in the chemical composition, especially in the amounts of silica, which varied from 27 to 50 per cent. Formulæ proposed at different times show the following variations:—$H_4Fe_6Al_{24}Si_{12}O_{68}$ (Rammelsberg); $H_4Fe_6Al_{24}Si_{11}O_{66}$ (Friedl); $H_4Fe_4Al_{24}Si_{10}O_{62}$ (Coloranio). From a consideration of the analyses of Friedl and Coloranio, Groth suggests the simple formula of a basic orthosilicate $(AlO)_4(AlOH)Fe(SiO_4)_2$. That this formula is correct is well established by careful analyses made by the authors. These gave the following mean results :—

	SiO₂.	Al₂O₃.	FeO.	H₂O.	Sp. gr.
St. Gothard..	27·70	55·04	15·07	2·19	3·748
Windham, Maine	27·60	55·75	14·43	2·20	3·728
Lisbon, New Hampshire .	27·44	55·16	15·72	1·68	3·775
Burnsville, N. Carolina..	27·47	55·83	14·74	1·96	3·773

From a comparison of the analyses with the results required by the formula, it will be observed that the silica is uniformly a trifle high. The authors are of opinion that quartz is an impurity in the mineral, and that it is present as very minute inclusions.   B. H. B.

Physiological Chemistry.

Calorimetry.   By A. D. WALLER (*Proc. physiol. Soc.*, 1893, 25—29).—The ordinate of a thermographic curve may be taken as an index to the rate of heat discharge per area per time, and the area of a thermographic variation can be expressed in calories. For practical

comparisons, the area of such a variation may be taken as that of a triangle with time as base and maximum ordinate as height.

From this, the idea sprang that for clinical purposes an ordinary thermometer might be employed for calorimetry. A mercurial manometer with an excursion of 5 mm. per 1° indicated the increased heat discharge (for instance, that consequent on muscular exertion) far better than a partial calorimeter surrounding a limb. Loss of heat by evaporation is separately estimated.

The calorimetric value of surface thermographic or thermometric readings was estimated by experiments with an india-rubber sphere containing a known weight of cooling water, readings being taken at intervals from internal and external thermometers. A third thermometer gives the temperature of the air.

The rate of cooling is not strictly proportional to the temperature difference (T.D.), but more precisely to $(T.D.)^{1\cdot233}$; but the discrepancy is slight, and in any case easily corrected in a graduation scale.

The following numbers represent the state of heat emission from a human fore-arm with a superficial area of 500 cm²., after rest and after exertion. The surrounding temperature was 20°, and the evaporation gauged as described below.

	After rest.	After exertion.
T.D.	12°	14°
i.c. heat emission ..	75 cals. per minute	90
Moisture..........	4 mgrs. per 20 cm². per minute	30
i.c. heat emission ..	6 cals. per minute	45
Total	81 cals. per minute	135

The water is estimated by means of shallow glass capsules, in the bottom of which calcium chloride solution had been evaporated to dryness. The capsule is weighed before and after it is inverted for a given time over an area of the surface of the body. With an external temperature of 20°, the following values (in milligrams, per 20 cm². per 10 minutes) were observed. Palm of hand, 24; sole of foot, 12; forehead, 12; cheek, 6; axilla, 10; popliteal space, 10; forearm, 5; leg, 5. W. D. H.

Asphyxia. By H. KRONECKER and JORDI (*Proc. physiol. Soc.*, 1893, 21—23).—The primary object of respiration is either to supply the organism with oxygen or to remove carbonic anhydride from it. A frog's heart will work as effectively when supplied with blood freed from its gases or with oxygenated blood; on the other hand, blood containing carbonic anhydride interferes with the heart's action, finally paralysing it. The heart beats again on removal of the carbonic anhydride (McGuire). Fishes can recover from asphyxia if opportunity be afforded to the blood of freeing itself from carbonic anhydride, by combination with substances introduced into the surrounding medium (Traube-Mengamic). Gold fish can live for two days and a half in a litre of water entirely shut off from air, and for about a day in boiled water. If, then, they are, in a dying condition,

conveyed to another litre of boiled out water, they recover, and survive 10—17 hours. Fresh fish introduced into the water tenanted by the dead fish live for some hours; but when a little sodium hydroxide is added they live a whole day. Fish die in water charged with carbonic anhydride, the amount of gas varying directly as the rapidity of death.

Further experiments, performed on the person of one of the authors, were designed to determine how much carbonic anhydride can be supported in inspired air. The gaseous mixture was inhaled from a gasometer of 40 litres' capacity. Equal parts of air and carbonic anhydride caused spasm of the glottis, and consequent inability to breathe at all. 30 per cent. of carbonic anhydride was breathed for a minute, the aspect of the subject of the experiment being dyspnœic; 22 per cent. of the gas caused less inconvenience; and a proportion of 8 per cent. caused much more ample breathing than normal. It was also found that an increase in the amount of carbonic anhydride produced in the body, as by the ascent of a tower, caused considerable stimulation of the respiratory efforts, and in one experiment voluntary maximum inspirations were continued for an hour.

W. D. H.

Respiratory Exchange in Rabbits. By M. S. PEMBREY and A. GÜRBER (*J. Physiol.*, **15**, 449—463).—The gases were analysed by Haldane's method. Rabbits were found to vary considerably in the amount of gases exchanged and in the respiratory quotient. The chief point investigated in the present paper is the influence of bleeding and transfusion on the gaseous interchange; and it was found that severe bleeding, even if half of the animal's blood is removed, whether followed by transfusion or not, causes no decrease in the respiratory exchange, provided the animal's nutrition does not suffer from the operation. If, however, the hæmoglobin is reduced to one-third of its normal value, the animal dies in convulsions. The experiments present another proof that vital combustion processes occur chiefly in the tissues of the body, not in the blood. W. D. H.

Gases in the Air-Bladder of Fishes. By C. BOHR (*J. Physiol.*, **15**, 494—500).—The gas in the air-bladder of fishes is a true secretion of a highly oxygenated gaseous mixture. The secretion appears to be under the control of the nervous system, and it fails when the branches of the vagus nerve which supply the air-bladder are cut.

W. D. H.

Action of Digestive Ferments on Nucleïn Compounds. By P. M. POPOFF (*Zeit. physiol. Chem.*, **18**, 533—539).—A calf's thymus was divided into three parts. Part 1 was subjected to artificial gastric digestion for one hour. The undissolved residue contained 2·56 per cent. of phosphorus; the filtrate 0·243.

Part 2.—Here digestion went on for two hours. The percentage of phosphorus was then 2·66 in the residue.

Part 3.—Here digestion went on for three hours. The percentage of phosphorus in the residue was then 2·9.

A similar experiment with pancreatic fluid showed a much more rapid solution of the phosphorus-containing substance. So probably,

though but little nuclein is digested in the stomach, a considerable quantity is absorbed after pancreatic digestion in the intestines.

W. D. H.

Nuclein in Nutrition. By GUMLICH (*Zeit. physiol. Chem.*, **18**, 508—512).—The nuclein used was obtained from the thymus gland, and was given to dogs, the urine of which was examined. The effect was not marked, except in producing an increase in the phosphoric acid. There was no increase in the uric acid. W. D. H.

Nuclein Bases in the Body. By Y. INOKO (*Zeit. physiol. Chem.*, **18**, 540—544).—The amounts of various bases derived from nuclein were estimated in various organs (testis, pancreas), and in spermatozoa of various animals. It was found in all cases that xanthine bases are more abundant than sarkine bases, but the relation between them varies. Of the xanthine bases, those rich in oxygen (hypoxanthine and xanthine) are more abundant than those rich in nitrogen (adenine and guanine), the proportion varying from 2 : 1 to 3 : 2.

W. D. H.

Hepatic Glycogensis. By D. NOËL PATON (*Proc. Roy. Soc.*, **54**, 313—318).—Much recent research has tended to show that Bernard's original teaching concerning the glycogenic function of the liver is correct. The question whether the change of glycogen into sugar is due to a ferment action, or to the vital action of the liver cells is, however, undecided, and the object of the present paper is to elucidate this point. The question is considered how far the process is dependent on the life of the liver cell. The excised organ, roughly minced, was kept at 37—40° in normal salt solution, and it was found that during the first half hour the loss of glycogen was very rapid; after that it went on more slowly. In other experiments the liver substance was killed by grinding it with sand. These, compared with control specimens in which the liver was roughly minced, showed a much slower disappearance of glycogen. The histological changes occurring in the liver cells are also described. The conversion of glycogen into sugar is divisible into two periods : (1) an early period of rapid conversion occurring before obvious structural changes are seen in the cells ; (2) a late period of slow conversion after these changes have developed. The rapid and extensive changes occurring in the first period is inhibited by destroying the cells, and is due to their vital activity ; the second slower stage is believed to be due to the action of an enzyme.

The influence of various agencies in distinguishing between the two processes is next described ; namely, of a temperature of 60°, which inhibits vital but not the fermentative activity—and of sodium fluoride (1 per cent. solution), which acts similarly.

Chloroform was found to increase hepatic amylolysis markedly ; and it is the early rapid amylolysis which is accelerated, the microscope revealing a more rapid katabolic change in the cells than the normal. Some experiments performed during life show that chloroform anæsthesia then increases hepatic amylolysis also.

Ether acts like chloroform but in a smaller degree. Pyrogallic acid

(0·25 per cent. solution) acts in the same way. Morphine, curare, amylic nitrite, and sodium salicylate have no action.

The development, after death, of an acid reaction, due in part to lactic acid, is not the cause of amylolysis. The influence of micro-organisms is also excluded.

In the first rapid amylolysis, glucose is formed; intermediate substances of the nature of dextrins and maltose were not detected. In the later amylolysis, dextrins (and possibly maltose) were always found.   W. D. H.

Chemistry of Muscle. By H. BORUTTAU (*Zeit. physiol. Chem.*, **18**, 513—524).—The glycogen of heart muscle diminishes after death more rapidly than that of skeletal muscles under the same conditions. Heart muscle or its aqueous extract changes glycogen into sugar more rapidly than skeletal muscle or its aqueous extract. The original percentage of glycogen in the fresh heart muscle is about the same as in skeletal muscle.

Inosite is more abundant in heart muscle than in skeletal muscle. Heart muscle is neutral in reaction; when tetanised, or after death, it turns acid.   W. D. H.

Elastic Substance of the Aorta. By H. SCHWARZ (*Zeit. physiol. Chem.*, **18**, 487—507).—Elastin was obtained from the aorta by taking advantage of its relative indigestibility in artificial gastric juice. It is identical with that obtained from the *Ligamentum nuchœ*. Elastin contains sulphur, which is removable by boiling with 1 per cent. potassium hydroxide; this, however, does not destroy the elastin, which still retains its characteristic properties. With super-heated steam, it yields hemi-elastin and elastin-peptone (proto- and deutero-elastose). Decomposed by hydrochloric acid, it yields ammonia, hydrogen sulphide, leucine, glycocine, tyrosine, homologous benzoic acids, and lysatinin. By fusion with alkali, it yields, among other products, indole, skatole, benzene, and phenol.   W. D. H.

Chemistry of Leucocytes. By L. LILIENFELD (*Zeit. physiol. Chem.*, **18**, 473—486).—The leucocytes were obtained from the thymus gland by the use of pressure and the centrifuge. The aqueous extract contained a proteïd coagulating at 48° and another coagulating at 73—75°. A nucleo-albumin was also obtained by Halliburton's method; it was found to contain C, 53·46; H, 7·64; N, 15·57; and P, 0·433 per cent. The alcoholic extract of the cells contained protagon, amidovaleric acid, inosite, and mono-potassium phosphate.

A nucleïn-containing proteïd, called nucleo-histon, was obtained by precipitating with acetic acid an aqueous extract of the cells. [This is what Wooldridge termed " tissue-fibrinogen."—Abstractor.] Its elementary composition is C, 48·46; H, 7·0; N, 16·86; P, 3·025; S, 0·701 per cent. The action of artificial gastric juice, or of 0·8 per cent. hydrochloric acid, on this is to separate the nucleïn from the proteïd, which goes into solution as peptone. The nucleïn contains

4·991 per cent. of phosphorus. Nucleïc acid prepared from this contains 9·94 per cent. of phosphorus.

Histon, the other constituent of nucleo-histon, was first obtained from birds' red corpuscles by Kossel (*Zeit. physiol. Chem.*, 1884), who described it as a peptone-like substance; many have since regarded it as an artificial product, formed by the acid used in its preparation. This view is combated in the present paper. Leucohiston, however, differs from Kossel's compound in being coagulable by heat.

The following table gives the quantitative composition of leucocytes.

Water	88·51
Solids	11·49

100 parts of the solids contain—

Total phosphorus	3·01
Total nitrogen.....................	15·03
Proteid	1·76
Leuconuclein......................	68·78
Histon	8·67
Lecithin	7·51
Fat	4·02
Cholesterol........................	4·40
Glycogen	0·80

The weight of the silver compounds of the nucleïn bases (adenine, hypoxanthine) obtained was 15·17. W. D. H.

Fluorine in Bones and Teeth. By S. GABRIEL (*Zeit. anal Chem.*, **33**, 53—54).—To the conclusion arrived at by Gabriel (Abstr., 1893, ii, 82), that teeth contain only traces of fluorine, Wrampelmeyer has objected, on the ground that organic substances cannot be incinerated without loss of fluorides. The author replies that it is impossible to assume the loss of 1 per cent. of fluorine; that the results obtained by Brandl and Tappeiner (Abstr., 1893, ii, 23) tend to negative any important loss on incineration; that his own results do not depend entirely on the examination of the ash of teeth, but also on the extraction of the powdered bone with alkaline glycerol; and, lastly, that his communication, above quoted, was only a preliminary one, the whole subject being exhaustively treated later, (this vol., ii, 21). M. J. S.

Composition of the Liver Fat of "Birgus latro." By E. GÉRARD (*J. Pharm.*, [5], **28**, 443—450).—The purified fat obtained from this crab melts at 24°, and gives, by saponification, glycerol and a mixture of fatty acids melting at 26° to 27°. Of these, the acids which form barium salts soluble in hot water, are lauric, caproic, and caprylic. The other acids are stearic and palmitic. The mixture contains cholesterol, but no unsaturated acids. W. T.

Colour of Lepidopterous Larvæ. By E. B. POULTON (*Proc. Roy. Soc.*, **54**, 417—430).—Previous researches having shown that

probably certain elements of the colouring of butterflies' larvæ are modified chlorophyll (metachlorophyll), derived from the food plant, a critical experiment is now described. The larvæ of *Try-phæna pronuba* were arranged in three sets, fed respectively on (1) the yellow, etiolated leaves from the heart of the cabbage; (2) the white mid-ribs of such leaves, from which the yellow blades were carefully removed; and (3) the deep green external leaves. Those in the first and third sets became green or brown, those in the second set remained colourless, but the greater number died during the experiment.   W. D. H.

Nature and Causes of the Green Colour of Oysters. By A. CHATIN and A. MUNTZ (*Compt. rend.*, **118**, 17—23 and 56—58).— Oysters, as Berthelot stated some years ago, do not contain chlorophyll, but they contain iron, which is concentrated chiefly in the gills, where the green colour is deepest, and amounts to from 0·06 to 0·08 per cent. of the dry matter. In the rest of the oyster, it amounts to from 0·025 to 0·048 per cent. It is noteworthy that in brown oysters the percentage of iron is practically the same, and it is likewise concentrated in the gills, where the brown colour is deepest. The mud at the bottom of the cultivating tanks contains in 1000 parts : N, 0·79 to 1·92; P_2O_5, 0·75 to 2·10; SO_3, 6·33 to 34·18; Cl, 3·44 to 23·71 ; I, 0·0005 to 0·005; CaO, 5·60 to 110·60 : Fe_2O_3, 17·04 to 77·79. In two cases, the nitrogen is as high as 6·22 and 7·55, respectively; in one, the phosphoric anhydride is as low as 0·15, and in another, 0·43 ; in two cases, the calcium oxide is 219·8 and 213·36 respectively. The muds contain a considerable quantity of iron in the form of ferrous oxide and ferrous sulphide. When the mud is exposed to air during the summer months, in accordance with the usual practice, its black colour gradually changes to brown, the ferrous sulphide and oxide being oxidised, and the ammoniacal nitrogen converted into nitrates. Part of this oxidation is due to the action of algæ, which develop rapidly under the influence of light, and decompose the carbonic acid in the water, liberating nascent oxygen in contact with the ferrous compound.   C. H. B.

Potassium Thiocyanate in the Stomach. By G. KELLING (*Zeit. physiol. Chem.*, **18**, 397—408).—It is shown that potassium thiocyanate is present in the stomach contents ; it may be recognised by the ferric chloride reaction, and presumably comes from the swallowed saliva. The amount of hydrochloric acid in the stomach makes a difference in the reaction. If saliva is mixed with dilute hydrochloric acid, carbonic anhydride comes off, and the ferric chloride reaction is weaker. On the addition of stronger hydrochloric acid, the intensity of the reaction increases in time.

The presence of potassium thiocyanate is a source of error in Uffelmann's reaction for lactic acid.   W. D. H.

Secretion of Myxine Glutinosa. By E. W. REID (*J. Physiol.*, **15**, 488—493).—The slime of this fish contains two substances, a granule substance and a thread substance (Abstr., 1893, ii, 429) ; the

former was dissolved in 0·01 per cent. solution of potassium hydroxide, leaving the threads unaffected; the granule substance was precipitated from solution, either by 1 per cent. solution of acetic, or 0·1 per cent. of hydrochloric, acid.

The granule substance resembles mucin in many of its characters; it, however, yields no reducing substance on treatment with sulphuric acid. It, moreover, contains phosphorus, although it is completely soluble in artificial gastric juice.

The thread substance appears to be a more insoluble variety of the same material. It is insoluble in gastric juice, but is stated to contain less phosphorus than the granule substance; accurate quantitative experiments are, however, not given. W. D. H.

Excretion of Nitrogen in Diabetes. By H. LEO (*Chem. Centr.*, 1893, ii, 603; from *Zeit. klin. Med.*, **22**, 223—224).—In normal individuals, a test meal containing 75 grams of cane sugar, 50 grams of butter, and 120 grams of maize, causes a marked rise in the excretion of nitrogen. In diabetics, the same occurs, the rise in nitrogenous output running almost parallel with that of the volume of urine and amount of sugar therein. Shortly afterwards a fall occurs. The rise of nitrogen is, as a rule, more marked than in normal persons. In one case, an increase in the carbohydrates of the food led to a diminution in the urinary nitrogen; and, although the proteïd-sparing action of carbohydrates is not always seen in diabetes, it is the general rule. W. D. H.

Passage of Chloroform, administered by Inhalation, into the Urine. By P. VITALI (*L'Orosi*, **16**, 299—304).—Bréaudat (*J. Pharm. Chim.*, 1893, 194) was unable to find chloroform in the urine after its administration as an anæsthetic; the author, however, employing the very sensitive process given below, in some cases found traces of chloroform in the urine. A current of pure hydrogen is passed through the urine, or any other liquid containing chloroform; the latter is thus carried off as vapour, and on burning the hydrogen and allowing the flame to play on a piece of fine brass gauze, the wire assumes a bluish-white colour. On drawing off the products of combustion from the gauze, and passing them through ammonia solution, a bluish coloration is obtained, and the solution is found to contain chlorine. The quantity of chloroform found in the urine after inhalation of the anæsthetic is always very small, and in some cases none can be detected.

After administration of chloroform, the urine always reduces the solutions of Fehling, Trommer, and Böttger, and gives a white turbidity when boiled with mercuric chloride solution; this is not due to the presence of glucose. This result is in agreement with those obtained by Kast, v. Mering, and Zeller, but opposed to those of Bréaudat. The author also shows that, after inhalation of chloroform, the urine contains organic chlorine, although it does not seem to be present as trichloromethylglycuronic acid, or its homologue. W. J. P.

South Amerian Meat Extract and Meat Peptone. By E. KEMMERICH (*Zeit. physiol. Chem.*, **18**, 409—422).—The methods of analysing these preparations of the author are described.

The extract contains 15—18 per cent. of water, 6·19 of gelatin, 14·16 of albumoses, 12·31 of peptone, a total proteïd percentage of 33·23. There is also present 20 to 22·3 per cent. of mineral matters (chiefly phosphates), 1·22 of glycogen, 4·33 of creatinine, 0·25 to 1 of carnine, 1 of fat, 0·9 of ammonia, and 18 to 22 of other extractives.

The meat peptone contains more proteïd, 18·75 of soluble albumin and gelatin, 39·16 of albumose and peptone ; a total of 57·91.

The glycogen is present in well-preserved specimens made from fresh meat.

The presence of creatinine—not creatine—confirms G. S. Johnson's work (*Proc. Roy. Soc.*, **50**, 28). W. D. H.

Physiological Action of Pilocarpine. By A. CURCI (*Chem. Centr.*, 1893, ii, 659 ; from *Annali Chim. Farm.*, **18**, 3—8).—Pilocarpine produces hyper-secretion, convulsions, and paralysis. The paralysis is accounted for by regarding pilocarpine as a quaternary ammonium compound. But phenol and oximhydroxyl groups, the most powerful in producing hyper-secretion and convulsions, are absent. It is not improbable, however, that in the organism changes may occur, a pilocarpinate being formed with the bases of the body ; thus :—

$$C_5NH_4 \cdot CMe {<}^{CO-}_{NMe_3}{>}O + ROH = C_5NH_4 \cdot CMe(NMe_3 \cdot OH) \cdot COOR.$$
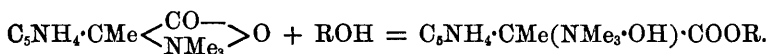
In dogs, the drug leaves the body in the urine partly as free pilocarpine and partly as such a pilocarpinate. W. D. H.

Crystalline Substance in Silkworms destroyed by Muscardine. By E. VERSON (*Staz. Sper. Agrar.*, **24**, 245—255).—The disease known as " Muscardine," and caused by *Botrite Bassiana*, gives rise to a crystalline efflorescence on the dead silkworms. This efflorescence was examined by Brugnatelli, at the instance of Dandolo. In a note by Dandolo (1814), the substance is stated to consist chiefly of magnesia, phosphoric acid, and ammonia. After describing the appearance of the substance under different atmospheric conditions, the author gives in detail his method of purification and analysis. The following results were obtained: water lost at 100°, 12·635 ; oxalic acid, 48·975 ; ammonia, 22·365, and magnesia, 1·9 per cent. These numbers point to the formula, $C_2O_4Mg,5C_2O_4(NH_4)_2 + 10H_2O$. The action of *Botrite Bassiana* is probably limited to the production of oxalic acid, a small portion of which is neutralised by magnesia, whilst most of it combines with the ammonia liberated in the decomposition of the silkworm. N. H. M.

Chemistry of Vegetable Physiology and Agriculture.

Action of Calcium Sulphite and of Hydrogen Potassium Sulphite on Alcoholic Fermentation. By F. RAVIZZA (*Staz. Sper. Agrar.*, **24**, 593—609).—The want of agreement of the results obtained by Czeppel (*Boll. Soc. Viticoll.*, 1890, 625, and 1892, 47) and those of Chiaromonte (this vol., ii, 61) is shortly discussed. In the first experiments, now described, must (sp. gr. 1·0768), containing a solution of invert sugar and an excess of tartaric acid, was treated with varying amounts of calcium sulphite (0·05 to 0·5 per litre), the temperature and amounts of carbonic anhydride evolved being observed daily. Under the conditions of the experiments, with a temperature of 30°, the sulphite had no effect, either in lowering the temperature or in increasing the activity of the ferment. The next experiments were similar to the first, but hydrogen potassium sulphite was employed instead of the calcium salt, and the temperature was much lower (14°). With 0·05 and 0·15 gram of sulphite there was less evolution of carbonic anhydride for the first two weeks than when no sulphite was added; but after that the amounts were much the same. With larger amounts of sulphite, the fermentation was stopped. A third series of experiments was made in which the effect of calcium sulphite was directly compared with that of hydrogen potassium sulphite, both at 35° and at 15°. At the higher temperature, 1·2 gram of calcium sulphite per litre and 0·3 gram of the potassium salt were practically without effect; 0·5 gram of hydrogen potassium sulphite stopped the fermentation. At 15°, the amounts of calcium salt employed were almost without effect after a few days; 0·30 gram of the potassium salt retarded the fermentation somewhat, even to the end, whilst 0·5 gram, as at 35°, stopped it altogether.

Experiments were made to ascertain the effect of the two salts on saccharomyces, by determining the number of colonies from 1 c.c. of wine at different dates after treatment with 0·01 gram per litre of each salt. Without any addition the number of colonies increased in 15 days to about 20 times the original number; with the calcium salt, the number was reduced to about a seventh, whilst with hydrogen potassium sulphite the number was reduced to almost nothing (oneseventieth).

The results of the author's experiments are opposed to those obtained by Czeppel (*loc. cit.*), and resemble Chiaromonte's. As regards hydrogen potassium sulphite, it is much more active than calcium sulphite, and, when further studied, will be probably substituted for it in the treatment of wines, whether to subdue the fermentation, or to give wine a greater power of resisting hot summers, or for sending wines to distant countries. Before recommending its use, however, more experiments should be made with natural musts.   N. H. M.

Formation of Carbonic Anhydride and Absorption of Oxygen by Leaves after their Removal from Plants. By BERTHELOT and G. ANDRÉ (*Compt. rend.*, **118**, 45—54 and 104—112).—When

leaves of wheat, hazel (*Corylus avelana*), and *Sedum maximum* are heated at 100—110° in a current of hydrogen, carbonic anhydride is evolved in quantity amounting to about 0·7 per cent. of the dry matter. The evolution of gas takes place in two stages, namely, at 94—99°, and at 110° after desiccation is practically complete. In a current of air instead of hydrogen, the phenomena are similar, carbonic anhydride being evolved in two stages corresponding respectively with the evolution of the greater part of the water, while the temperature inside the flask is about 100°, and with the period when leaves have become practically dry, and the temperature of the flask has risen to about 110°. The quantity of carbonic anhydride evolved is greater than in a current of hydrogen.

If similar leaves are immersed in water and heated at 100° in a slow current of air, the quantity of carbonic anhydride evolved in the case of wheat is greater than in the previous experiments with a current of hydrogen, but less than with a current of air. It would seem that the oxygen under the conditions specified is only able to act on the leaves after it has dissolved in the water. With hazel leaves, the results are similar to those obtained in hydrogen, and with leaves of *Sedum maximum* the quantity of carbonic anhydride given off is greater than in the previous experiments with either air or hydrogen.

The moist leaves were heated at 100°, in a closed vessel filled with oxygen, and the amounts of carbonic anhydride formed and oxygen absorbed were determined. It was found that the volume ratio, O_2/CO_2, was 1·32 for wheat, 1·60 for hazel, and 1·90 for *S. maximum*. The quantity of carbonic anhydride formed is in all three cases much greater than in hydrogen. The quantity of oxygen absorbed without production of carbonic anhydride is greatest in the case of hazel leaves, and least with the leaves of *S. maximum*, and it is noteworthy that the former contain the lowest and the latter the highest proportion of water.

When these leaves are allowed to dry gradually at the ordinary temperature, the quantity of carbonic anhydride given off is much greater than at 100—110°. The leaves of *S. maximum* dry very slowly, and the phenomena are complicated by the development of *mucidinæ* towards the close of the operation. The increased evolution of carbonic anhydride during drying is due to biological processes. Some carbon is evolved in the form of volatile compounds, the nature of which has not yet been determined. The nitrogen and the ash, however, remain unchanged in amount throughout the process. The hydrogen is eliminated, either in the form of water or of other compounds in which the ratio of hydrogen to oxygen is the same. Practically, the whole of the oxygen in the carbonic anhydride evolved is derived from the air, and not from the leaves, and hence the formation of carbonic anhydride is not due to the action of anærobic ferments. The volume ratio of carbonic anhydride evolved to oxygen absorbed is practically unity, as in the respiration of animals.

When moist leaves are placed in a vessel filled with oxygen at the ordinary temperature, so that the leaves do not become dry, carbonic anhydride is evolved, and oxygen is absorbed, and at first these

changes seem to be due chiefly to the internal reactions of the leaves, but, after a time, moulds develop, and produce special effects of decomposition and slow combination. During the first week, the volume ratio, O_2/CO_2, is practically unity, but afterwards oxygen is absorbed in excess of that corresponding with the carbonic anhydride. With hazel leaves, if the action of the oxygen is prolonged, the weight of carbonic anhydride formed may rise as high as 41 per cent. of the weight of the substance, whilst the weight of oxygen absorbed is as high as 70·3 per cent. Neither alcohol nor acetic acid is formed. The nitrogen remains unchanged in amount.

In all cases, it would seem that the phenomena are due to the breaking up of several of the primary glucogenic molecules, which are the generators of the carbohydrates present in the leaves, the carbon being converted into carbonic anhydride, and the hydrogen into water, just as in the nutrition of animals. The quantity of heat developed by these changes is about one-fourth of the heat developed in the animal organism, as measured by the rise of temperature that it is capable of producing in the body undergoing oxidation.

<div align="right">C. H. B.</div>

Method of Investigating the Exchanges of Gases between Living Organisms and the Surrounding Atmosphere. By BERTHELOT (*Compt. rend.*, **118**, 112—114).—The animal or plant is enclosed in a vessel so large that the normal course of respiration, &c., is not interfered with, and from time to time known volumes of gas are expelled by introducing known volumes of air, and the expelled gas is analysed. In the case of the action of air on leaves, for instance, the carbonic anhydride is absorbed by potassium hydroxide.

If the capacity of the vessel is V, and the total weight of the gas to be estimated is at a particular time, p, then, if a very small bubble of air is introduced, v, and is allowed to diffuse uniformly through the vessel (that is, the current of air must be very slow), a volume of gas, v, will be expelled from the vessel. This volume will contain a weight of the gas to be estimated, $p\dfrac{v}{V}$, and there will remain in the vessel $p\left(1 - \dfrac{v}{V}\right)$. After n bubbles the quantity remaining will be $p\left(1 - \dfrac{v}{V}\right)^n$. Assuming that $nv = V$, and v being very small, it follows that

$$p(\tfrac{1}{2} - \tfrac{1}{6} + \tfrac{1}{24} - \tfrac{1}{120}\ldots.) = 0·368\ldots.p,$$

and after m similar operations $p\,(0·368)^m$ practically. Divergences from these ratios indicate that some absorption or evolution of gas is taking place; and it is clear that since the removal of the gas for analysis in no way interferes with the course of the experiment, the investigation may be carried on continuously.   C. H. B.

Nitrates in Living Plants. By DEMOUSSY (*Compt. rend.*, **118**, 79—82).—Berthelot and André showed that nitrates are always present in plants, and pointed out their importance to vegetation

(compare also Dehérain, this vol., ii, p. 156). The power of retention of nitrates by living plants, and the absence of such power in the case of dead plants, is shown by the following experiment:—Some meadow-grass, including tops and roots, was divided into three lots of 100 grams (22 grams of dry matter). The first sample was kept for 24 hours in cold water. At the end of this time, the plant was distinctly coloured by diphenylamine sulphate, whilst the water only contained 0·1 milligram of nitrogen. On extracting the substance with boiling water, 21·9 milligram of nitric nitrogen was obtained. The second sample was dried and then extracted with hot water; 22·6 milligrams of nitric nitrogen was obtained, whilst the root no longer gave any reaction with diphenylamine sulphate. The third portion was subjected for an hour to the action of chloroform vapour, and then kept for 24 hours in cold water (1 litre). The root gave only a very slight reaction with diphenylamine, and none at all after being washed a little. The extract contained 21·3 milligrams of nitric nitrogen.

Notwithstanding their solubility, nitrates are held by the protoplasm with an energy comparable with chemical affinity. Dead leaves and roots become easily deprived of nitrates by rain; but Berthelot frequently found considerable amounts of nitric acid in above ground portions of plants which died during a period of dry weather.

N. H. M.

Copper in Various Parts of the Vine. By F. SESTINI (*Staz. Sper. Agrar.*, **24**, 115—132).—The first plants examined had been watered with a solution of copper sulphate. The plants grew well in the spring, but became sickly in the summer, and died in the autumn. This was possibly due to injury by the large amount of mineral manures, phosphates, sodium nitrate, &c., applied; but probably their destruction was largely due to the copper salt. The air-dried roots contained (1) 0·0547 and (2) 0·1307 per cent. of copper, whilst a portion of the stem (without leaves) contained only 0·0013 per cent. Four samples of leaves of plants which had not been treated with copper salts contained respectively 0·00047, 0·00056, 0·00060, and 0·00054 per cent. of copper. New shoots of vines, which had been treated with copper about three months previously, contained 0·00073 per cent. of copper; the leaves contained 0·00063, and the tendrils 0·00011 per cent. New shoots from other plants contained 0·00053 per cent., whilst the older leaves contained 0·00118 per cent. of copper.

Most of the copper found in vines will be in those portions to which it was directly applied, as there is very little circulation within the plant; consequently, those portions which are not directly treated with copper salts will contain only about the quantity usually found in vines to which no copper has been applied.   N. H. M.

Cane Sugar in Seeds of Plants, Raffinose in Wheat Germs, Crystalline Lævulin. By E. SCHULZE and S. FRANKFURT (*Ber.*, **27**. 62—64, 64—65, and 65—66).—The cane sugar is obtained from the alcoholic extract of the seed, by precipitation as the strontia compound, and the precipitate is then decomposed by carbonic anhydride,

and treated according to the method already described by the authors (*Landw. Versuchs-Stat.*, **34**, 408).

By this method the authors have obtained cane sugar from the seeds of *Triticum vulgare, Secale cereale, Avena sativa, Polygonum fagopyrum, Cannabis sativa, Helianthus annuus, Pisum sativum, Soja hispida,* and *Coffea arabica.*

Cane sugar has also been obtained from the seeds of *Vicia faba, Phaseolus vulgaris, Hordeum distichum, Zea mays, Arachis hypogœa, Corylus avellana, Juglans regia,* and *Amygdalus communis;* so that it is very widely distributed in seeds. The only seeds which gave a negative result were those of *Lupinus luteus.*

The authors confirm the result of Richardson and Crompton, who found cane sugar in wheat germs (*Ber.,* **19**, 1180).

Cane sugar was also obtained from the green shoots of the pea.

Raffinose is obtained from wheat germs by evaporating the sugar solution obtained by the above method to a syrup, and extracting the cane sugar with the requisite quantity of boiling alcohol. When the syrupy residue is mixed with absolute alcohol, a precipitate of raffinose is obtained. The product, after purification by recrystallisation, gave for a 10 per cent. aqueous solution $[\alpha]_D = +105\cdot5$; and, on oxidation with nitric acid, $22\cdot2$ per cent. of saccharic acid.

A carbohydrate which has all the properties of lævulin is obtained, together with cane sugar, from the stalks of rye gathered before the formation of seed commences. It is isolated in the same way as raffinose, from wheat germs. It crystallises in small prisms, and when dried over sulphuric acid forms a white powder, which quickly takes up water from the air; on analysis, it gave numbers corresponding with the formula $C_{12}H_{22}O_{11}$. It reduces Fehling's solution only after heating with an acid, and is optically inactive in aqueous solution. E. C. R.

Lecithin in Vegetable Substances. By E. SCHULZE and S. FRANKFURT (*Landw. Versuchs-Stat.,* 1893, 307—328).—To obtain lecithin from seeds, they should be finely ground, treated with ether, and extracted with 50—60 per cent. alcohol, the alcohol evaporated, and the residue treated with ether; water should now be added to saturation, and the emulsion which is thus formed must be cleared by the addition of salt; after separation, the ether is evaporated, and the lecithin which is left, is purified by redissolving it in alcohol. To work quantitatively, the phosphoric acid must be determined in the alcoholic extract, and the lecithin calculated therefrom (factor: magnesium pyrophosphate $\times\ 7\cdot2703$). Full details are given, as also the percentage of lecithin in many seeds. E. W. P.

Sunflower Cake. By T. KOSUTANY (*Landw. Versüchs-Stat.,* 1893, 253—263). Sunflowers (*Helianthus annuus*) are largely grown in Hungary. The oil is expressed from their seeds, and the cake thus obtained is used as fodder for cattle. A vast number of seeds from all parts of the world have been analysed, and the constituents are found to vary considerably. Taking one sample only out of the many: the dried seed gave nitrogenous matter, $15\cdot98$; fat, $36\ 6$; non-

nitrogenous extract, 19·39; fibre, 24·3; ash, 3·13 per cent.—air-dried seed (husked): water, 14·7; nitrogenous substance, 24·95; fat, 49·62; non-nitrogenous extract, 4·18; fibre, 3·28; ash, 3·27 per cent. The methods of preparing the cake and expressing the oil are described. E. W. P.

Pumpkin-seed Cake. By T. KOSUTANY (*Landw. Versuchs-Stat.*, 1893, 264—269).—Several analyses of the whole fruit of plants of different varieties of pumpkins are given. The dried seeds contain 41·1—53·96 per cent. of oil; the oil is largely used as food, and for burning. E. W. P.

Composition of Winter Drainage from bare Soil and Soil sown with Wheat. By P. P. DEHÉRAIN (*Compt. rend.*, 117, 1041—1045; compare Abstr., 1893, ii, 338 and 486.)—In a previous paper, the amounts of nitric nitrogen collected early in 1892 from the Grignon vegetation cases were given; the present paper gives the results obtained with drainage from November, 1892, to March, 1893. The summer drainage from fallow soil contained 145 parts of nitric nitrogen per million, whilst in the four winter months it only contained an average of 92 per million—in December 183 and 157, in January 11 and 9, in February 78, and in March 116 per million. When the loss of nitrogen is calculated per hectare, it is found to be very great, being 81·185 kilos. in winter and 221·8 kilos. for the whole year, or nearly five times as much as the loss of nitrogen observed at Rothamsted (47 kilos. per hectare). This great difference is due to the trituration of the Grignon soil, and the aeration which it underwent when put into the cases. A considerable diminution in the amounts of nitrates formed has already been observed. Thus, the drainage of December, 1893, contained only 93 parts of nitric nitrogen per million.

With regard to the loss from bare soil, as compared with soil covered with vegetation, a second case sown with rye-grass only lost 10·3 kilos. of nitrogen per hectare, as against 81·185 kilos. lost by fallow land; and the drainage contained only 13 parts of nitric nitrogen per million. Inasmuch as there was no reason to suppose that there was any essential difference in the nitrification of the two cases, it seemed likely that the nitric acid was retained by the plants. An examination of gramineous plants grown in the garden of the museum and in a Grignon meadow showed that the dry roots contained 0·062 and 0·375 per cent. of nitric nitrogen respectively, whilst the stems contained 0·113 and 0·039 per cent. These plants have, therefore, the power of storing up nitrates during the winter months for future use.

The richness of grass land in nitrogen, and the increase in richness observed at Grignon (from 1·5 per cent. in 1879 to 1·88 in 1888), is due partly to the nitrogen-fixing organisms (Berthelot), to cryptogamic vegetation (Schlœsing, jun., and Laurent), and partly to the abstraction of nitrates from the water percolating through it.

Not only the ordinary grasses, but also wheat has the power of retaining nitrates in the winter; thus roots taken from the field in December contained 0·563 per cent. of nitric nitrogen (in the dry matter), whilst roots and stems taken from a bank next the field

contained respectively 1·041 and 0·187 per cent. The roots were at this time over 30 cm. long.

From March, 1892, to March, 1893, the four cases with bare soil lost 221·4, 193·1, 242·1, and 245·2 kilos. of nitrogen per hectare. Grass land lost in the same time only 30 kilos., and soils bearing successively beet and winter wheat lost 19·4, 17·6, and 40·6 kilos. per hectare. These comparatively slight losses are due to the much lessened drainage, and, as shown above, to the retentive power of the plants.

<div align="right">N. H. M.</div>

Influence of Iron on Barley. By P. PETIT (*Compt. rend.*, **117**, 1105—1107).—Barley was grown in sand freed from iron, to which the necessary ash constituents were added. There were four series of pots :—No. 1 had 0·00604 milligram of iron in the form of barley nucleïn (4 grams; see Abstr. 1893, i, 539); No. 2 had 0·98 gram of iron as ferrous sulphate (5 grams); No. 3 had 0·999 gram of iron as ferric sulphate (4·4 grams); No. 4 had no iron at all. Nucleïn and ferrous sulphate were both beneficial, whilst ferric sulphate acted as a poison. The following amounts of produce, dried at 50°, were obtained in each of the four series.

	I.	II.	III.	IV.
Stems	3·55	3·72	0·80	2·77
Leaves	5·29	3·88	0·81	3·95
Total produce for 1 gram of seeds..	48	40	9	39

The greatest increase was produced under the influence of the nucleïn.

The dry matter of the stems and leaves contained the following percentage amounts of nitrogen, ash, and iron.

	Stems.			Leaves.		
	N.	Ash.	Fe.	N.	Ash.	Fe.
I	1·44	20·5	0·24	2·24	20·1	0·25
II	1·49	19·5	0·51	2·01	19·8	0·57
III	1·48	19·2	0·48	2·2	17·9	0·56
IV	1·31	20·5	0·05	1·81	16·9	0·05

As regards the stems, the amount of nitrogen was slightly increased by the nucleïn and iron salts, whilst the iron was very greatly increased. In the leaves, the nucleïn had a very marked effect on the nitrogen percentage.

<div align="right">N. H. M.</div>

Analytical Chemistry.

Colorimeter with Lummer-Brodhun Double Prism. By H. KRÜSS (*Zeit. anorg. Chem.*, **5**, 325—329).—In colorimeters it is, of course, of the greatest importance that the two fields to be compared should be as close together as possible. This is generally effected by means of two reflection prisms cemented together below the eye-piece. By this means the two fields are made to form the two halves of the field of vision. However closely the prisms are cemented together the line of contact is not a mathematical line, and, being magnified by the eyepiece, forms a dark line across the field of vision, thus preventing the formation of an unbroken field, and reducing the delicacy of the apparatus. The author has overcome this difficulty by the introduction of a Lummer-Brodhun double prism. This double prism consists of one ordinary total reflecting prism, with a perfectly plane hypothenuse surface, and one with the hypothenuse surface spherical, with only a small (circular) plane surface in the centre. This second prism is adjusted to the first, so that its plane circle is in the centre of the plane hypothenuse side of the other, and the two are pressed together so tightly that no air remains between the two plane surfaces in contact. In this way, a double prism is obtained in which light rays striking the contact surfaces pass through without change, whilst those striking the remaining portion of the plane hypothenuse surface are totally reflected. The arrangement of prisms, and the construction of the Lummer-Brodhun double prism will be readily seen from the annexed sketch. In this, AB is the Lummer-Brodhun
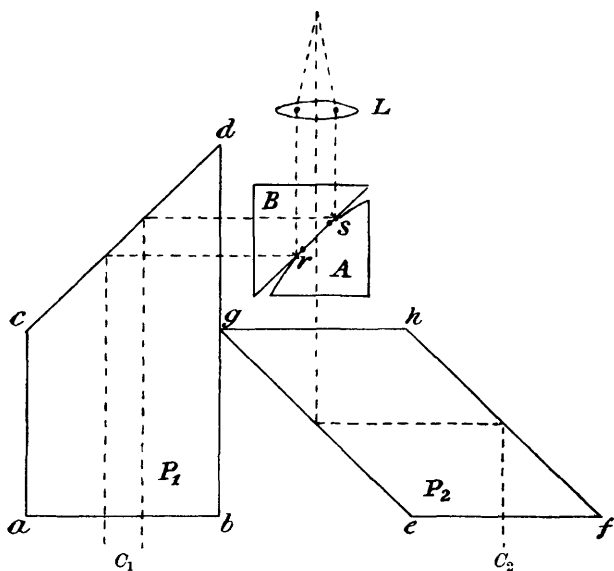
double prism, L the lens of the eyepiece, and the dotted lines C^1 and C^2 the path of the light rays from the two colour surfaces to be compared. By this arrangement C^2 is seen as a circle in the centre of the field of vision, C^1 as an annular space surrounding that centre. When the two colours are exactly equalised, there is no visible line of demarcation between the two surfaces, and greater accuracy is obtainable than heretofore. The combination of prisms is so arranged that each light ray has to pass through an equal distance of glass and be reflected an equal number of times, so that the two fields are maintained of equal brightness.   L. T. T.

Estimation of Bromine in Urine. By A. NICOLLE (*J. Pharm.*, [5], **28**, 298—299).—The residue from the evaporation of 50 c.c. of urine to which has been added 2 grams of potash is heated to dull redness. The aqueous extract is made up to 40 c.c., and distilled with 20 grams of potassium dichromate and 10 c.c. of sulphuric acid, the distillate being collected in a bulb-tube containing 20—25 c.c. of a 4 per cent. solution of potassium iodide. The distillation is continued for about 15 minutes after the apparent conclusion of the evolution of bromine. The liberated iodine is titrated in the usual manner with sodium thiosulphate. If sulphur is present, the urine is boiled with barium chloride and hydrochloric acid, and filtered before evaporation ; or, better, the aqueous extract, after incineration, is boiled with oxalic acid so long as hydrogen sulphide is evolved. If the urine contains iodides, the aqueous extract is neutralised and the iodine expelled by boiling with potassium dichromate, the sulphuric acid is then added and the distillation continued as usual.
                                                              W. T.

[*Note by Abstractor.*—Iodine is not completely expelled by boiling with the proportions of dichromate and solution given above. Chlorine is liberated at the same time as the bromine, to the extent of more than 3 per cent. of the quantity present.]

Microchemical Examination for Iodine. By G. DENIGÈS (*J. Pharm.*, [5], **28**, 499—500).—The iodoform reaction is used and the precipitate examined microscopically for the characteristic hexagonal plates of iodoform. To apply the test, a solution is prepared containing the iodine as sodium or potassium salt. If in the form of iodate, it is reduced by the addition of a drop of sodium hydrogen sulphite solution. If the solution is very dilute, about 10 c.c. is taken, a drop of soda solution added, and then five or six drops of a 10 per cent. solution of acetone ; finally, a solution of an alkali hypochlorite is added drop by drop.   W. T.

Test for Free Sulphur. By J. C. GIL (*Zeit. anal. Chem.*, **33**, 54—55).—On adding an alkali polysulphide, or a solution of sulphur in an alkali hydroxide, to hot alcohol, which has been boiled long enough to expel all air, a blue colour is gradually developed. On cooling the blue colour disappears ; it is, however, restored by reheating, if oxygen, or any other substance which decomposes polysulphides, has been expelled, otherwise not. 0·4 milligram of *hepar*

sulphuris will colour 50 c.c. of 96 per cent. alcohol.   To use the test for the detection of free sulphur, the substance is added to boiling alcohol containing a trace of potash.   M. J. S.

Toxicological Detection of Phosphorus. By J. v. D'HAGEN and P. WOLTERING (*Chem. Centr.*, 1893, ii, 1103—1104; from *Ned. Tydschr. Pharm.*, **5**, 335—343).—The authors mention a case of supposed phosphorus poisoning in which the phosphorus could not be proved by *post-mortem* appearances, or by the conventional chemical analysis.   On distilling, however, the contents of the large intestine in a current of carbonic anhydride, gases containing phosphorus were given off.   The authors did not venture to decide whether or no these gases were caused by a putrefactive process.   L. DE K.

Toxicological Detection of Phosphorus. By H. W. BETTINK and F. C. E. v. EMBDEN (*Chem. Centr.*, 1893, ii, 1104; from *Ned. Tydschr. Pharm.*, **5**, 343—345).—The authors failed to detect phosphorus in the body of a man eight days after death.   Traces of hypophosphorous acid and hydrogen phosphide could, however, be detected in every distillate.   As the deceased had been medically treated with hypophosphites, the finding of volatile phosphorus compounds did not positively point to a poisoning with phosphorus. To throw some light on the case, the authors carefully searched for arsenic, as this is nearly always contained in commercial phosphorus, but rarely, if ever, in hypophosphites.   They succeeded in demonstrating the presence of arsenic in the fatty-degenerated liver.

L. DE K.

Employment of Ammoniacal Mercuric Cyanide in Quantitative Analysis. By F. W. SCHMIDT (*Ber.*, **27**, 225—238).—In the quantitative estimation of metals precipitated as sulphides much time is consumed in converting the sulphides into oxides by redissolving in acids and precipitating with alkalis; the author has, therefore, endeavoured to devise a method of bringing about this conversion in one operation.   The first attempt consisted in heating the washed sulphide with an excess of precipitated mercuric oxide, but the results obtained in this way were always too high, the oxide formed invariably containing basic sulphate; the formation of the latter may be avoided by using, in place of the oxide, a mixture of 1 part of mercuric nitrate and 2 parts of mercuric oxide, and the results then obtained in the case of copper and zinc sulphides agree very closely with the theoretical numbers.

A much more convenient method is to treat the moist sulphide with a cold saturated solution of mercuric cyanide in ammonia; the metallic sulphide is thus converted into cyanide with simultaneous formation of mercuric sulphide, and on ignition the latter is volatilised, and the cyanide decomposed, leaving the metal, which is converted into oxide by the oxygen of the air.   The moist sulphide and filter are placed in a weighed crucible, the whole just covered with the ammoniacal mercuric cyanide solution, carefully evaporated to dryness, and ignited.   The results obtained in the case of copper,

zinc, bismuth, and iron show a very close agreement with the calculated numbers.

Ammonia and mercuric cyanide combine to form the crystalline compound $Hg(CN)_2,NH_3$, and, when this is heated alone, it, unlike mercuric cyanide, does not yield any difficultly volatile paracyanogen, so that no error from this source is to be feared. The commercial mercuric cyanide should be recrystallised two or three times before dissolving in ammonia; or the amount of non-volatile matter in the solution may be determined and allowed for.   H. G. C.

Volumetric Estimation of Calcium, Strontium, or Barium. By VIZERN (*J. Pharm.*, [5], **28**, 442—443).—The neutral solution of the salt is titrated with a standard solution of sodium carbonate, using phenolphthaleïn as indicator. The process cannot be used in presence of other bases giving precipitates with carbonates.
                                                            W. T.

Estimation of Lead.   By LINDEMANN and MOTTEU (*Bull. Soc. Chim.*, [3], **9**, 812—819).—Metallic sulphides are completely peroxidised by bleaching powder solution, the sulphur being oxidised to sulphate.   Since peroxides in the presence of hydrochloric acid liberate their equivalent of iodine from potassium iodide, their amount may be estimated volumetrically.

In the case of galena free from foreign metals, the powdered mineral ($0.5 — 1.0$ gram), moistened with bleaching powder solution, is ground into an extremely fine mud, more bleaching powder solution (30—40 c.c.) is added, and then dilute hydrochloric acid (5 per cent.), gently warming until the liberated oxides are dissolved, the slow evolution of chlorine ensuring the oxidation of the last traces of sulphates.   Enough bleaching powder solution to completely peroxidise the lead is now added to the product, and the peroxide collected, purified, and treated with excess of potassium iodide (25 c.c. of 5 per cent. solution) and hydrochloric acid (30 c.c. of 20 per cent. acid).   The liquid is diluted (to 150—200 c.c.), and, after due agitation, the liberated iodine is titrated with sodium thiosulphate.   2 mols. of thiosulphate are equivalent to 1 atom of lead.

In the presence of metals other than copper, the lead is best precipitated as sulphide from the product of the action of bleaching powder on the mineral, and the sulphide treated as above.   In the presence of copper, the copper sulphide simultaneously precipitated may be removed by means of potassium cyanide.

Lead carbonate and oxides are converted into the nitrate before treatment.   The basic and peroxide oxygen of red lead may be estimated by treating it with nitric acid (sp. gr. 1.2).   The undissolved peroxide and dissolved monoxide are then separately estimated; the total lead may also be estimated as a check.

Numerous results are quoted, which agree well amongst themselves, and fairly well with those obtained by the sulphate gravimetric method.   JN. W.

Quantitative Analysis by Electrolosis. By A. CLASSEN (*Ber.*, **27**, 163—165).—Lead is precipitated as dioxide, and a reguline

deposit is obtained in the presence of a sufficient quantity of nitric acid. The solution is warmed to 50—60° and a current of 1·5—1·7 ampères employed. About 1 5 grams of dioxide can be precipitated in three hours. If lead and copper are present in the same solution, 98—99 per cent. of the lead is precipitated in one hour with a current of 1·1—1·2 ampères. The current is then stopped, and the solution washed into another platinum dish, ammonia added, and the cold mixture electrolysed with a current of 1—1·2 ampères, when the copper, together with the remainder of the lead, is precipitated in about 3—4 hours.   E. C. R.

Quantitative Analysis by Electrolysis. By O. PILOTY (*Ber.*, **27**, 280—282).—In view of the adverse criticism to which Classen's electrolytic methods of quantitative analysis have been recently subjected, the author publishes a table of the experimental results obtained by him with these methods, showing that a high degree of accuracy can be thus attained.   A. H.

Analysis of Steel. By L. SCHNEIDER (*Chem. Centr.*, 1893, ii, 623—624; from *Österr. Zeit. Berg. Hütt.*, **41**, 365—368).—*Estimation of Sulphur.*—The author dissolves the sample in hydrochloric acid and passes the hydrogen sulphide through a solution of potassium permanganate. No sulphur is detectible in the residue. It is not advisable to expel any air from the apparatus by means of hydrogen, as this gas is difficult to free from sulphur. *Estimation of Silicon.*—As no silicon hydride is formed on dissolving steel in hydrochloric acid, the residue from the sulphur estimation may be safely used for the silicon estimation. The author does not follow the old plan of evaporating to dryness and taking up again with hydrochloric acid, but evaporates the liquid with sulphuric acid until sulphuric fumes appear. The residue is boiled with water until all the ferric sulphate has dissolved, and, after the silicic acid has been collected, ignited, and weighed, it is evaporated with hydrofluoric acid to ascertain its purity.   L. DE K.

Colorimetric Estimation of Small Quantities of Vanadium in the Presence of Large Quantities of Iron. By V. v. KLECKI (*Zeit., anorg. Chem.*, **5**, 374—380).—With the aim of finding an easy method of determining vanadium in the presence of excess of iron, the author has investigated the action of a large number of reagents on vanadium solutions. A sulphuric acid solution of vanadic acid was employed. A large number of substances giving coloured compounds with vanadic acid also give colorations with iron salts, and are, therefore, useless for this purpose. Another class of substances (such as papaverine, meconine, quinine sulphate, &c.) give colour reactions with vanadic acid and not with iron, but the tint and degree of colour depend so much on degree of dilution, temperature, &c., as to be of little value. Dextrose appears to be the only substance that answers at all for this purpose. With greatly varying strength of acid, the colour varies with this between blue and green. If, however, the solution is made to contain only about 10 per cent.

of sulphuric acid, a pale green coloration is obtained, which varies approximately with the quantity of vanadium present, and forms a useful rough mode of estimation. It is not, however, very delicate, and the limit of error may reach as much as 8 per cent. of the vanadium present. L. T. T.

Separation of Vanadic acid from Chromic acid. By V. v. KLECKI (*Zeit. anorg. Chem.*, **5**, 381—382).—The author finds that a modification of Carnot's method of estimation of vanadic acid by precipitation as ammonium uranium vanadate (Abstr., 1887, 897) forms a good means for the separation of vanadic from chromic acid, the corresponding chromium precipitate being dissolved by the addition of even a single drop of acetic acid. Excess of uranium nitrate is added to the neutral solution containing the vanadic and chromic acids. A few drops of acetic acid are then added, the whole boiled, and filtered. The precipitate, after strong ignition, is weighed as $V_2O_5,2UO_3$. Very good results are obtained. L. T. T.

Detection and Approximate Estimation of Sand in Food Stuffs, Meal, &c. By A. EMMERLING (*Zeit. anal. Chem.*, **33**, 46—48). —A solution of 1000 parts of crystallised zinc sulphate in 725 parts of water has, at ordinary temperatures, a sp. gr. of 1·43. A test tube is half filled with this solution and then filled nearly to the top with water, without admixture of the two layers. The substance to be tested is stirred into the water without disturbing the heavy liquid. The organic substances sink only to the surface of the zinc solution, the sand to the bottom of the tube.

For quantitative purposes, a special funnel-shaped vessel is used, to the neck of which is attached, by caoutchouc tubing, a graduated tube, each of whose divisions contains 0·2 gram of sand. The funnel is 10 cm. diameter at the top and has an angle of 35°, with a cylindrical neck 17 cm. long and ·3 cm. diameter, tapered at its lower end at an acute angle to the diameter of the graduated tube. It is filled with the zinc solution to the top of the cylindrical neck, water is added nearly to the edge of the funnel, and 20 grams of material is used for each experiment, so that each division of the graduated tube corresponds with 1 per cent. of sand. In the event of the presence of calcium carbonate, the contents of the graduated tube can be treated with acid, washed, incinerated, and weighed. M. J. S.

Spirit Assaying by Weight. By J. SCARISBRICK (*J. Soc. Chem. Ind.*, **12**, 893—901).—The author has constructed tables which are suitable for use with a gravity bottle or any other instrument capable of ascertaining specific gravities from 1·000 to 0·790. They have been built from the invaluable material of Gilpin and Blagden ; but, for spirits of great alcoholic strength, the numbers obtained by Tralles, Fownes, Drinkwater, and Squibs have been utilised. For the standard alcohol, Sikes's proof spirit at 15·5° has been adopted. The general principle proceeded on in building up the system is the recognition of weights and not volumes, as weight does not change with temperature, but volume does, particularly in the case of alcohol.

The system proposed by the author answers for the purpose of identifying the spirit, is easily understood, and quickly applied, furnishes accurate numbers for assessment at all temperatures, and satisfies the wants of all concerned. L. DE K.

Detection of Glucose and Cane Sugar in Honey. By O. HAENLE (*Zeit. anal. Chem.*, **33**, 99—103). Genuine honey from flowers contains no dextrin, or only traces; it rotates the plane of polarised light to the left. A dextrorotatory specimen is adulterated with starch-sugar syrup if it exhibits the dextrin reaction, but with cane sugar if dextrin is absent.

The honey from conifers, which is always brown, contains dextrin; before dialysis it rotates the plane of polarised light to the right; after dialysis it is optically inactive. A suitable dialyser for the removal of the diffusible constituents is figured and described. It consists of a shallow, wooden box, in which the tray of parchment paper is supported on parallel laths, whilst a slow stream of water flows below it. To detect dextrin, a solution is made of 1 part of the honey (first clarified by warming and stirring) in two parts of water. This solution is decolorised by warming for five minutes with 2 per cent. of animal charcoal. 5—10 c.c. is placed in a test tube and covered with a layer (2 c.c.) of absolute alcohol. A turbidity at the zone of contact indicates dextrin. Although the author's own numbers show that the optical rotation of pure honey is not constant, he gives the following formulæ for determining the amount of adulteration.

For starch sugar in honey from flowers, $x = \dfrac{3P + p}{10}$.

For ,, in honey from conifers, $x = \dfrac{3P - p}{10}$,

where P is the rotation of the honey solution, $(1:2)$, p is the rotation of genuine honey $(= 30)$, and x is the percentage of starch sugar syrup. For cane sugar syrup the divisor 10 is replaced by 4.

The validity of the author's conclusions is, however, disputed by numerous investigators. M. J. S.

Test for " Saccharin " in Presence of Salicylic acid. By HAIRS (*Chem. Centr.*, 1893, ii, 987; from *Apoth. Zeit.*, **8**, 500).—The isolated mixture containing " saccharin " and salicylic acid is acidified with hydrochloric acid and then mixed with excess of bromine water, which causes the complete precipitation of the salicylic acid. The filtrate from the dibromosalicylic acid is freed from bromine by a current of air and then agitated with ether. The latter on evaporation with a few drops of sodium hydrogen carbonate, leaves a residue of " saccharin," which may be recognised by its sweet taste and other well-known reactions. The author made a successful test experiment with 0·1 gram of " saccharin " and 0·05 gram of salicylic acid dissolved in 200 c.c. of claret. L. DE K.

Estimation of Hydrogen Cyanide in Cherry-Laurel Water, &c. By G. DENIGÈS (*J. Pharm.*, [5], **29**, 10—15).—When aqueous hydrogen cyanide is titrated with silver nitrate, the silver cyanide redissolves so slowly, especially in dilute solutions, as to obscure the end of the reaction; whilst when the acid is previously neutralised, the slightest excess of alkali retards the appearance of the final precipitate. These difficulties may be obviated by using potassium iodide as indicator, in solutions made strongly alkaline with soda or ammonia. With cherry-laurel water, for instance, the liquid (100 c.c.) is treated with ammonia (10 c.c.), and also with alcohol (5 c.c.) if hydrobenzamide be precipitated; a little potassium iodide is then added, and, finally, decinormal silver nitrate, until a distinct turbidity of silver iodide appears. The end-point is quickly and sharply determined: 1 c.c. of decinormal silver nitrate $= 0.0054$ gram of hydrogen cyanide. Hydrocyanic acid is neutralised with ammonia or soda, and sufficiently diluted before titration. Potassium cyanide is titrated in about 0·1 per cent. solution, with the addition of ammonia (10 c.c. to each 100 c.c.). Alkaline sulphides, if present, are first decomposed by ammoniacal zinc sulphate. The test analyses quoted are satisfactory. JN. W.

Estimation of Hydrocyanic acid. By G. GREGOR (*Zeit. anal. Chem.*, **33**, 30—45).—When estimating gravimetrically as silver cyanide, the precautions to be observed are that the measured quantity (50 c.c.) of the liquid (bitter-almond, or laurel water, or a solution of the acid itself, so far diluted that no loss from volatilisation will occur during the measuring out) is mixed in a stoppered bottle, first with 5 c.c. of 1·73 per cent. ammonia, and then with a very small excess of silver nitrate solution. Nitric acid is then added to very feeble acidity. Since acid of 0·6 per cent. already dissolves traces of silver cyanide, this degree of acidity must not be exceeded. All the above operations must be performed in the cold, and with the greatest rapidity; a delay of a few minutes causes a loss in the result. Water is added to 200—300 c.c., the precipitate caused to aggregate by shaking, washed, dried, and ignited.

Of volumetric methods, Liebig's, Vielhaber's, and C. Mohr's, have, in the author's as in other hands, given higher numbers than the gravimetric. Volhard's method, carried out as follows, gives results closely agreeing with those obtained by weighing. 100 c.c. of the solution is mixed in a $\frac{1}{4}$-litre flask with 5 c.c. of ammonia, 50 c.c. of N/10 silver nitrate is added, and then immediately nitric acid, free from nitrous acid, to slight acidity. After making up, and shaking, 50 c.c. of the filtrate, mixed with a few drops of ferric sulphate, and, if necessary, with more nitric acid, is titrated with N/10 thiocyanate. M. J. S.

Extraction of Fat. By L. GEBEK (*Landw. Versuchs Stat.*, 1893, 193—206).—The author first shows that the usual method of estimating fat in fodders is not trustworthy, by reason of the dissolution of substances other than fat by the ether. He then recounts his experiments, wherein he mixed gypsum and bone charcoal with the substance to be analysed, the results not being wholly satisfactory;

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finally he used Spanish earth, a red-brown powder containing chalk, but the latter must be removed, otherwise lime salts of the fatty acids would be formed—for this purpose the earth is levigated with water on a large porcelain dish, sulphuric acid is added, and the mass then thoroughly dried; the hardened mass is afterwards broken up and passed through a sieve with $1\frac{1}{2}$—2 mm wide mesh, and then heated to redness in a platinum basin.

Five grams of the substance are then mixed with 10—15 grams of the earth and placed in the extraction tube over a plug of wadding fitted into a narrowing of the lower part of the tube; this tube should be 14 cm. long, of which the upper 8 cm. are 2·5 cm. wide, the remainder 1 cm., the whole terminating in a still narrower tube, 2 cm. long; it is at the top of this last that the plug of wadding is placed. The ether which percolates is colourless, and leaves a colourless residue on evaporation, except when chlorophyll is present in the substance. To obtain good results, it matters not whether the ether be dry or not, but the substance itself must be air-dried only. E. W. P.

Comparison of the Various Methods in Use for the Estimation of Milk Fat. By GRAFFENBERGER (*Landw. Versuchs Stat.*, 1893, 247—252).—The various methods in use have been carefully examined, and the author points out the defects of each; he seems to consider Soxhlet's the most exact, as he has used that as the criterion for all the others—all give too low results. Apart from Soxhlet's, Schmidt's and Gottlieb's are the best, whilst Gerber's method is the worst. Schmidt's and Gottlieb's tally well with one another, but Schmidt's is the most rapid to work. Gerber's and Demichel's can only be considered to be preliminary methods; consequently, the author recommends the methods of Schmidt and Gottlieb as being, taking everything into consideration, exact, the most rapid, and the cheapest. E. W. P.

Estimation of Ergot in Meals and Brans. By H. LAUCK (*Landw. Versuchs Stat.*, 1893, 303—305).—10 grams of the sample is mixed with 20–30 c.c. of ether which has been distilled over sodium; then, after the addition of 1·2 c.c. of 5 per cent. sulphuric acid, and thorough shaking, the mixture is allowed to remain for six hours, after which it is filtered, washed with ether, and the filtrate made up to 40 c c. in a test tube, or cylinder, marked at the 40 c.c. It is then mixed with 1·8 c.c. of a saturated solution of sodium hydrogen carbonate, when, after thorough mixing, a violet-coloured portion separates at the bottom of the tubes, and the percentage of ergot present is estimated by the depth of the tint produced Standard tints are prepared beforehand. Ergot loses its colour by age. E. W. P.

Estimation of Urea. By E. RIEGLER (*Zeit. anal. Chem.*, **33**, 49—53).—Urea is decomposed by Millon's reagent, with evolution of equal volumes of carbonic anhydride and nitrogen. The theoretical volume of gas for 1 gram of urea is 744 c.c. (at 0° and 760 millimetres), but the average of numerous experiments gives 724 c.c.,

with such small variations that, by applying the corresponding factor the error will not exceed 0·5 per cent. The decomposition is effected in an ordinary test tube ($6 \times \frac{3}{4}$ in.), 1 c. of the urea solution being taken. The reagent is prepared by dissolving 10 c.c. of mercury in 130 c.c. of nitric acid of 1·4 sp. gr., adding 140 c.c. of water, and, if necessary, filtering. Of this solution, 2 c.c. is run in by a funnel tube, and, when the first tumultous evolution of gas is over, the mixture is heated to boiling several times. The gases are received in some form of gas volumeter and reduced to normal conditions, including the correction for aqueous vapour. The number of c.c. of gas, multiplied by the weight of 1 c.c. of nitrogen and by 1·1, gives the weight of urea in grams.　　　　　　　　　　　　　　　　　　　　　　　M. J. S.

Reactions with Potassium Mercuric Iodide, and with Iodine dissolved in Potassium Iodide. By TANRET (*J. Pharm.*, [5], **28**, 433—441 and 490—499).—*Reactions with alkaloïds.*—The author summarises the work done on this group, and gives a table showing, for 19 alkaloïds, the comparative delicacy of the reactions given by Mayer's, Valser's and Bouchardat's solutions. From numerous experiments of his own, he draws the following conclusions :—(1) Valser's solution precipitates the non-volatile alkaloïds equally well from acid, neutral, or slightly alkaline, solutions. (2) The reaction is much more sensitive with the salts of the volatile alkaloïds than with the free bases. (3) For some salts of volatile alkaloïds—for example, pelletierine sulphate and cicutine hydrobromide, the delicacy of Valser's reagent is much increased by the addition of a little soda. (4) Valser's and Bouchardat's solutions should only be used to test neutral solutions, as many substances other than alkaloïds are precipitated in acid solution.

Caffeïne is not precipitated by potassium mercuric iodide from solution in organic acids. In sulphuric acid solution, Mayer's reagent shows the presence of one-fiftieth, Valser's, of one six-hundredth, part of alkaloïd. Iodine in potassium iodide detects the presence of 1 part of caffeïne in 20,000 parts of a mineral acid solution; with acetic acid, the reagent is useless.

Theobromine is not precipitated by potassium mercuric iodide, but gives a black precipitate with Bouchardat's reagent.

Reactions with glucosides.—No glucoside is precipitated by potassium mercuric iodide from neutral or acetic acid solution. From solution in dilute sulphuric acid, Valser's reagent precipitates vincetoxin, convallamarin, aurantiamarin, digitaleïn, and amorphous digitalin (Codex).

The combination of glucoside and mercuric iodide is soluble in alcohol; ether dissolves the digitalin compound and decomposes the others.

Reactions with proteïds, &c.—Albumin gives a precipitate with potassium mercuric iodide in acetic acid solution. This precipitate is insoluble in excess of the reagent, in acetic acid, alcohol, ether, or solution of potassium iodide. For the detection of albumin in urine, 5 c.c. of the reagent is taken in a test tube, and the filtered urine added drop by drop. A bluish disc at the contact surface of the two

liquids is observed when the quantity of albumin per litre of urine is 0·01 gram or over.

In acid solutions, peptones give precipitates which show properties much resembling those of the alkaloïd precipitates. Ether causes the disappearance of the precipitate from dilute solutions; more bulky precipitates collect into a sticky mass. In either case the ether decomposes the precipitate, and does not re-deposit the compound on evaporation, as is the case with most of the alkaloïd precipitates. Peptones partially prevent the formation of precipitates with alkaloïds in neutral solution, rendering the reaction much less delicate.

Solutions of 1 part of gelatin in 180,000 react with potassium mercuric iodide in acid solution. The reaction is less sensitive with iodine in potassium iodide. The mercurial precipitate is insoluble in ether, but soluble in alcohol and in hot acidified water. The gelatin precipitate collects together, forming a characteristically elastic mass.

An acetic acid solution of caseïn gives a precipitate with potassium mercuric iodide which is insoluble in excess of the hot reagent, but soluble in alcohol. W. T.

Separation and Estimation of the Cacao Alkaloïds. By W. E. KUNZE (*Zeit. anal. Chem.*, **33**, 1—29).

—The processes hitherto employed (see Abstr., 1893, ii, 198) have been directed exclusively to the estimation of the theobromine, whilst ignoring altogether the presence of caffeïne, and the wide divergences between their results may in part be attributed to the fact that in some of the methods both alkaloïds would be obtained, whilst in others the caffeïne would be more or less perfectly excluded. The following method, based on proof tests at each stage, estimates both alkaloïds. 10 grams of the cacao is boiled for 20 minutes with about 150 c.c. of 5 per cent. sulphuric acid, and the soluble matters are thoroughly washed out with boiling water. The warm extract is precipitated with a large excess of phosphomolybdic acid, and, after 24 hours, the precipitate is collected and washed with about a litre of 5 per cent. sulphuric acid. The filter containing the moist precipitate is treated in a beaker with excess of baryta in the cold, and carbonic anhydride is passed through the solution until all the baryta is thrown down. The whole is then thoroughly dried on the water-bath and extracted with boiling chloroform; the chlorororm is distilled off, and the two alkaloïds are left as a perfectly white residue, containing only a negligible trace of ash. The residue is weighed, dissolved in ammonia, and the solution heated to boiling. A considerable excess of silver nitrate (about 1·3 parts of silver for 1 part of theobromine) is added, and the boiling is continued until ammonia no longer escapes, and the liquid is reduced to a few cubic centimetres. Under these circumstances, an insoluble silver substitution-product of theobromine, $C_7H_7AgN_4O_2$, is obtained, whilst caffeïne forms no such derivative, and remains wholly in solution. The precipitate is collected and washed with boiling water. The silver in it may either be determined by ignition or by dissolving in nitric acid and precipitating as chloride (in the latter method

the theobromine may be recovered from the filtrate for identification), but it is equally accurate and more rapid to employ a known excess of silver solution, and to estimate the excess in the filtrate by titration with N/10 thiocyanate solution (Volhard's method). Both the theobromine and caffeïne can then be recovered by neutralising the respective nitric acid solutions, evaporating to dryness, and extracting with chloroform.   M. J. S.

Estimation of Tannin. By P. SISLEY (*Bull. Soc. Chim.*, [3], **9,** 755—772).—Of the various processes devised for the estimation of tannin, those based on the precipitation by metallic salts or by gelatin are open to the objection that impurities are liable to be simultaneously thrown down, whilst that based on its oxidation by potassium permanganate is not available in the presence of organic impurities. If, however the tannin is first precipitated as the zinc salt, for instance, and the latter then oxidised with permanganate, trustworthy results may be obtained. The ammoniacal zinc acetate used for the precipitation is made by dissolving zinc oxide (40 grams) in hot dilute acetic acid (65 c.c. glacial acid, 50 c.c. water), and adding excess of ammonia (22° B. to 500 c.c.), the filtered solution being kept in a well-stoppered vessel. The tannin solution (50 c.c. of about 3·3 per cent.) is treated with the zinc solution (5 c.c.), and the precipitated zinc compound rapidly filtered and washed with aqueous ammonia (3 per cent.), by which means the gallic acid and other impurities are eliminated. The temperature must not be raised, or gallic acid will be also precipitated. The portion of precipitate adhering to the sides of the precipitating vessel is dissolved in dilute sulphuric acid (50 c.c., 1 to 5), and the remainder washed with this solution into a large porcelain basin (2 litres), and diluted to 1 litre with water. Indigo-carmine solution (50 c.c. of a 20 gram per litre solution of 20 per cent. paste) is now added, and standard permanganate, N/100, run in slowly (one drop per second to one drop per three seconds) until the colour of the liquid changes from green to dirty yellow. The titre of the solution having been determined by a separate experiment, the amount of tannin present can be calculated, since the amount of permanganate required to oxidise 63 grams of crystallised oxalic acid is capable of oxidising 41·57 grams of tannin. The process gives good results if the above details are closely adhered to, trial experiments with pure tannin alone and mixed with gallic acid and extractive matters of barks having proved quite satisfactory.

Some analyses of tannin-containing materials are given. Commercial tannin contains from 85 to 72 per cent. of tannin, Chinese gall nuts from 61 to 57 per cent., other gall nuts from 69 to 54 per cent., sumach from 19 to 12 per cent., and various commercial extracts of gall nuts and sumach from 44 to 12 per cent.   JN. W.

Estimation of Indigotin in Indigo. By F. ULZER (*Chem. Centr.*, 1893, ii, 597; from *Mitt. Technol. Gewerb.-Mus. Wien*, 1892, 215).— The author's method is independent of the other organic matters which accompany the indigotin, and therefore yields good results

even in indigoes of low percentage. About 1 gram of the very finely-powdered sample is boiled for 10 minutes with 50 c c. of 5 per cent. aqueous soda and 10 c.c. of hydrogen peroxide (concentration not given). After cooling, it is diluted to twice its volume with water, and filtered through a tared filter. The precipitate is washed with hot water, then with dilute hydrochloric acid (1 : 10), again with hot water, and finally with boiling alcohol until the filtrate is pale blue. The precipitate is then dried at 100°, weighed, and incinerated, in order to weigh and subtract the small amount of ash. If the alcoholic filtrate is evaporated to dryness, and the residue heated at 100° until constant, the amount of indigo-red is approximately found. Good indigo contains about 70 per cent. of indigotin and 3 per cent. of indigo-red.   A. H.

Estimation of Alizarin and Allied Colouring Matters. By W. P. DREAPER (*J. Soc. Chem. Ind.*, **12**, 977—979).—1 gram of the alizarin paste or 0·25 gram of the powder is put into a small flask and, after adding 10 c c. of a solution of sodium acetate (100 grams of the salt in a litre of water and 5 c.c. of acetic acid), the solution is roughly made up to 50 c.c. and mixed with 1 gram of barium sulphate. The flask is heated on a sand bath, and as soon as the liquid begins to boil, a solution of copper sulphate containing 0·0095 gram of copper oxide per c.c. is run in from a burette, until precipitation is complete. To test whether sufficient copper solution has been added to precipitate all the dye as copper lake, the end of a glass rod is from time to time dipped into the liquid and gently pressed on to a folded slip of filter paper, the slip afterwards being unfolded, and the under surface tested with potassium ferrocyanide.

The process will allow of the direct comparison of different samples by a numerical copper-oxide standard. Its accuracy is not likely to be disturbed by impurities other than substances that form colour lakes. Any reducing sugars will have no action, owing to the acid reaction of the solution.   L. DE K.

Detection of Copper Phyllocyanate in Green Preserves. By A. TSCHIRCH (*Zeit. anal. Chem.*, **33**, 103).—An alcoholic extract is evaporated to dryness, the residue washed with water, and then treated with concentrated hydrochloric acid. Pure chlorophyll gives a deep blue solution and a residue soluble, with brown colour, in ether, but, if copper phyllocyanate is present, the hydrochloric acid dissolves only a small quantity of a yellow substance, and the residue dissolves, with green colour, in alcohol. If dilute hydrochloric acid is added to the alcoholic extract, a green colour indicates copper, since, in its absence, the mixture is yellow.   M. J. S.

Action of Sodium Peroxide on Natural or Artificial Colouring Matter of Wines. By RUIZAND (*J. Pharm.*, [5], **29**, 17—19).— When sodium peroxide is added to red wine, oxygen is evolved at a rate proportional to the acidity of the wine, and the colour changes through dark maroon to pale yellow. Any precipitate produced by

the liberated sodium hydroxide is easily soluble in acid. The time required to effect decolorisation varies with the relative amount of sodium peroxide, from five minutes with 0·25 gram per 5 c.c., to five days with 0·01 gram, whilst with 0·005 gram per 5 c.c. decolorisation is incomplete after eight days. The process is slightly hastened by the addition of hydrochloric acid. The same results are obtained with a tartaric acid alcoholic solution of œnolin, the colouring matter of red wine.

Aniline and azo-dyes, such as are used in the sophistication of wine, are not affected by the peroxide in acid solution, so that their presence in wine may be detected by treating it (5 c.c.) with sodium peroxide (0·1 to 0·15 gram) for 20 minutes, and then acidifying with acetic acid. If the colour is not discharged, an artificial dye is present, and, since the natural colouring matter of the wine has been destroyed by the reagent, may be tested for in the usual way. Other vegetable colouring matters behave in the same way as the colouring matter of wine, and cannot be detected by this means.   Jn. W.

Detection of Bile Pigment in Urine. By A. Jolles (*Zeit. physiol. Chem.*, **18**, 545—557).—In addition to the well-known Gmelin's test for bile pigment in urine, there are several modifications and several other tests. In all, twenty are described in the present paper, and their relative delicacy ascertained. Of these, some half dozen are so little adapted to the purpose that it is necessary to add 10 per cent. of bile to the urine in order to obtain them; and only one (Rosenbach's) of the six modifications of Gmelin's test is as delicate as the original. This requires 5 per cent. of bile. Two out of the list are so delicate as to be given by 2 per cent. of bile. Of these, Rosin's test is one (*Berlin klin. Wöch.*, 1893, 106), and Hupperts' (*Arch. Heilk.*, **8**, 351, 476, 1887) the other.

Rosin's test consists in the grass-green ring, which appears on pouring dilute iodine tincture carefully on the surface of the urine.

Huppert's test is as follows:—8 to 10 c.c. of urine is precipitated with milk of lime and the precipitate collected; the latter is then treated in a test tube with alcohol containing sulphuric acid, and the acid liquid heated to boiling, when it becomes green or blue if bile pigment is present.   W. D. H.

Estimation of Urobilin in Urine. By A. Studensky (*Chem. Centr.*, 1893, ii, 668; from *St. Petersburger med. Woch.*, 1893, 283). —The process consists in extracting the urobilin by means of chloroform in the presence of copper sulphate and ammonium sulphate, and in the colorometric comparison of the coloured chloroform solution of urobilin with standard solutions. If the urine to be examined be shaken with chloroform in the presence of copper sulphate, the urobilin will not be entirely dissolved until after repeated shakings. If, however, after the addition of the copper sulphate, the urine be saturated with ammonium sulphate, which, according to Méhu, precipitates urobilin, the whole of the latter is at once taken up by the chloroform. Without copper sulphate, only a portion of the urobilin is dissolved. The process is carried out in

the following way :—20 c.c. of urine is treated with $\frac{1}{10}$ vol. of saturated copper sulphate solution, then saturated with crystallised ammonium sulphate, and 10 c.c. of chloroform added. The mixture is shaken for some minutes, and as soon as a copper-red layer of chloroform solution has settled, a portion of it is removed by a separating funnel, placed in a test-tube, and compared with a standard solution of urobilin in chloroform. This solution is prepared by extracting a considerable amount of urine which contains much urobilin in the manner described, evaporating the chloroform solution to dryness, washing with ether, and weighing the residue. A series of solutions is then made up from this residue, and these may be preserved, even as long as two months, if kept in the dark in closed vessels and covered by a layer of saturated solution of ammonium sulphate.   A. H.

Estimation of Albumin. By F. KLUG (*Chem. Centr.*, 1893, ii, 499).—For the estimation of albumin, the author mixes 2 c.c. of the liquid to be examined with concentrated aqueous soda, and adds 4 drops of a 10 per cent. copper sulphate solution. The carefully-filtered solution is then examined in a spectrophotometer, and the intensity of the biuret coloration determined. The results obtained are trustworthy, and the whole estimation may be made in a quarter of an hour. The estimation of albumin in urine may also be carried out in this manner as by means of an excess of copper sulphate the greater part of the colouring matters are precipitated. The amount of colouring matters may also be determined by Vierordt's method, and deducted from the total amount of colouring matter and albumin found by the author's method.   H. G. C.

Detection of Albumin in Urine. By A. OLLENDORFF (*Zeit. anal. Chem.*, **33**, 120—121).—The author confirms the value of Zouchlos' potassium thiocyanate test. It is capable of detecting 0·005 per cent. of albumin, and other constituents of urine, with the exception of propeptone, have no dsturbing influence.

After taking copaiba balsam, or sandal oil, the urine may contain resin acids, precipitable by nitric acid, and, therefore, liable to be mistaken for albumin. Treatment of the precipitates with alcohol fails to distinguish them, since both dissolve. Alexander recommends the use of the following tests :—2 or 3 drops of hydrochloric acid are added to 8—10 c.c. of urine; this precipitates the resin acids. If, on adding acetic acid, a precipitate is produced not soluble in excess, this consists of mucin. A sample is heated and mixed with one-third of its volume of nitric acid (strength not stated). Since both resin acids and mucin are redissolved under these conditions, a turbidity indicates albumin.   M. J. S.

General and Physical Chemistry.

Spectrum of Electrolytic Iron. By J. N. LOCKYER (*Proc. Roy. Soc.*, **54**, 359—361).—A series of photographs was taken of the part of the spectrum between the K and C Fraunhofer lines. Electrolytic iron of a very high degree of purity was employed, and the spectrum obtained by using this as the poles of an electric arc lamp. The results are compared with those previously obtained by Thalen, Kayper and Runge, and McClean, the agreement being in all cases satisfactory. Many lines occur in the spectra of the other observers, however, which are not indicated in these photographs. In many cases, they are probably due, and can be traced, to impurities in the iron used by them ; in other cases, however, they appear to be owing to differences in temperature, or to insufficiency of exposure of the photographic plates. Evidences were obtained of calcium and manganese in the specimen of electrolytic iron employed, as well as of very minute traces of other metals.   L. M. J.

Refractometric Researches. By J. F. EIJKMAN (*Rec. Trav. Chim.*, **12**, 268—285).—In a previous paper (Abstr., 1893, ii, 1), the author has shown that it is impossible to calculate correctly the molecular refractions of the initial terms of any homologous series making use of the atomic refractions deduced in the ordinary manner, although a constant difference exists between the refractions of the higher members of such a series, and this difference is equal to that observed in any other similar series. It is now shown that the dispersion is subject to like irregularities. It therefore appears that the molecular refraction of the variable term in any homologous series, say $-CH_2-$, is constant and independent of the character of the series ; and it would seem probable that, in like manner, the invariable end terms of the series have constant molecular refractions, independent of the nature of the series ; or, in other words, in any series $x(CH_2)_n x$, $y(CH_2)_n y$, and $x(CH_2)_n y$; the refractions for CH_2, x and y should be constants, and, when once known, the refractions of any term of a series of this form might be calculated. The author shows that, neglecting the initial terms of the series, the above supposition is correct, and that an excellent agreement between calculated and observed values for the molecular refractions can be obtained. Tables are given for the values of the refractions of different groups entering into the composition of homologous series.   H. C.

Relation of the Critical Coefficient to the Formula $\frac{n-1}{d}$. By R. NASINI (*Gazzetta*, **23**, ii, 576—587).—The relation between the refraction constants of a substance and its critical coefficient, k, or the ratio of its critical temperature expressed on the absolute scale, and its critical pressure, has been already indicated by Guye

(*Ann. Chim. Phys.*, [6], **21**, 206). He showed that $M = 1\cdot8\,k/R$, where M and R are respectively the molecular weight and the specific refraction for the ray of infinite wave-length calculated from the formula $\dfrac{n^2 - 1}{d(n^2 + 2)}$. The molecular weight of a substance at its critical point can thus be determined, and was found by Guye to be in general the same as in the gaseous state. The same author further stated that the critical coefficient of a substance is the sum of the critical coefficients of the atoms composing its molecule; the nature of the bonds between the atoms has to be considered, just as in the case of molecular refraction.

If the refraction formula of Gladstone and Dale holds as well as that of Lorentz and Lorenz, the value $\dfrac{M(A - 1)}{kd}$ should be a constant; A being the refractive index for infinite wave-length given by Cauchy's formula. The author has calculated this constant for a number of aliphatic compounds, and finds it to have the mean value 2·79; the constancy is, however, not quite so good as that obtained from Guye's formula.

The author therefore considers that Gladstone and Dale's formula suffers but little from Guye's deduction of the n^2 formula from the critical constants. W. J. P.

Relation between the Refractive and Rotatory Properties of Compounds. New Method for Determining the Specific Rotation of Optically Active Substances. By I. KANONNIKOFF (*J. pr. Chem.*, [2], **49**, 137—184).—By determining the angles of the rotation of the plane of polarised light, α_1 and α_2, and the angles of minimum deviation, ϕ_1 and ϕ_2, of solutions of different concentration, it is found that $\alpha_1 - \alpha_2/\phi_1 - \phi_2 = \text{constant} = A$, from which the differential equation $\dfrac{d\alpha}{d\phi} = A$ and the integration $\alpha = A\phi \pm B$ result.

The author used a prism of 60° angle and a polarimeter tube of 200 mm. The values obtained for a large number of optically active substances dissolved in different solvents are tabulated.

The value of the constants A and B is independent of ultimate composition and of similarity of chemical properties. Thus, whilst lactose and nicotine give nearly the same value for A, galactose and glucose give very different values for the same constant.

The constants are of different value when the same substance is dissolved in different solvents, but the relation B/A is nearly the same for every substance dissolved in the same solvent; so that this relationship, which may be termed C, depends solely on the solvent employed. For example :—

	B.	A.	$\frac{B}{A}$ or C.
Sucrose in water	268·23	11·40	23·52
Lactose ,, ...	229·63	9·73	23·60
Nicotine ,, ...	227·72	9·66	23·56
Nicotine in alcohol........	537·50	20·77	25·87

By dividing the above integration by A, it becomes $\alpha = A(\phi \pm C)$. Obviously, the determination of the value of C for different solvents adds another physical constant to those already available for ascertaining the relationship between structure and properties. The author gives a table showing this value for 63 different substances which were used as solvents for camphor, and, in a few cases, other optically active substances. Certain deductions are made from this table, such as that the introduction of CH_2 into a molecule increases the value of C for the compound by an amount varying from 0·46 to 1·35, and averaging 0·85; considerable deviation from the average is observed in the case of formic acid and methylic alcohol. The most important of these deductions is, in the author's opinion, that the value of C depends more on the constitution of the compound than on the number of the atoms in its molecule, and on the manner in which these are united. Since the last-named conditions are the chief factors on which the other physical properties of compounds depend, the new value will furnish a nearer insight into the relationship between constitution and properties than can the older constants.

The influence of double linking of carbon atoms on the value of C is next discussed, and the few values which have been obtained for aromatic compounds are correlated. The angle ϕ decreases with dilution in the fatty series, but increases in the aromatic series; consequently the equation is $\alpha = A\phi + B$, and B becomes a positive value for compounds of the aromatic series. The value of C for these compounds diminishes with increase of complexity, but the value of the coefficient y (see below) increases with the increased complexity.

It is to be noted that for the determination of C it is a matter of indifference whether the optically active compound is the solvent or the substance dissolved.

When the relationship between the specific rotatory power of optically active substances and the constants A and B is examined, it is found that the values $\dfrac{B}{[\alpha]_D}$ and $\dfrac{[\alpha]_D}{A}$ are constants for the same solvents, whatever the dissolved substance, so that $[\alpha]_D = Ax = B/y$, where x and y are coefficients depending purely on the nature of the solvent. Obviously, $C = xy$.

By using the known values of $[\alpha]_D$ for sugars, x and y are shown to be 5·60 and 4·20, respectively, for water. This new method for calculating the specific rotatory power is independent of a knowledge of the density and concentration of the solution. The coefficients x and y for the solvent being known, it suffices to determine the angles α and ϕ for a solution of the substance whose specific rotatory power is to be ascertained; to dilute this solution and again determine the angles α and ϕ; these data will serve for the calculation. In the table, the value of y for a large number of compounds is given.

In applying this method, the author has found some notable exceptions in which the calculated $[\alpha]_D$ is twice that which has been directly determined. For example, a solution of Russian turpentine in ethylic alcohol gives the values A = 5·40 and B = 137·00; the

values for x and y for ethylic alcohol being 5·16 and 5·00, respectively, $[\alpha]_D$ for this turpentine becomes 27·63°; the observed value is $[\alpha]_D = 27·89°$. But a solution of this turpentine in chloroform has $A = 30·80$ and B 999·79; the values for x and y for chloroform are 1·78 and 18·21 respectively, whence $[\alpha]_D = 27·43° \times 2$. Nicotine and coniine are also quoted as showing the same anomaly.

These cases remain unexplained, but some light on the subject has been gathered from a study of sugar solutions. It was found that whilst a number of inverted sugars gave the same values for $[\alpha]_D$ as were calculated on the hypothesis that this value should be the mean of those of the various constituents into which the sugars are known to be converted by inversion, there were a few cases in which the determined value for $[\alpha]_D$ was some multiple proportion of that calculated on the above hypothesis. Numerous experiments on mixtures of molecular quantities of sugars are quoted, and it is concluded that (1) the existing values for the specific rotatory power of sugars are inaccurate; (2) the specific rotatory power of a mixture of compounds in molecular proportion is the mean of the specific rotatory power of the constituents; and (3) in the cases in which the mean value of the specific rotatory powers of the constituents in such a mixture is a multiple or submultiple of the observed value, there has been an action between the constituents of the mixture (compare Berthelot's compound of dextrose and lævulose (Abstr., 1887, 24).

The last conclusion raises the question whether some dissociation or association may not explain the anomalous behaviour of Russian turpentine, nicotine, and coniine, referred to above. An investigation of tartrates also suggests a similar explanation. The following values for tartaric acid and metallic tartrates have been obtained :—

	$[\alpha]_D.$
Tartaric acid	$+12·46°$
Acid tartrate, $C_4H_5RO_6$	$+24·48$
Normal tartrates, $C_4H_4R_2O_6$	$+30·44$

Normal tartrates of the amines, in aqueous solution, divide themselves into three classes : (1) those which have the same value for $[\alpha]_D$ as have acid tartrates ; these are the tartrates of the more powerful bases, such as ethylamine, and must be regarded as being dissociated in the solution into acid tartrates and uncombined amine ; (2) those which have $[\alpha]_D = 18°$, such as isobutylamine tartrate ; these must be looked upon as being partly dissociated into acid tartrate and partly into free tartaric acid and free base ; (3) those which have $[\alpha]_D = 12°$; these dissociate in water completely into acid and base, and comprise the tartrates of the feeble bases, such as aniline.

In alcoholic solution, the tartrates of the more powerful bases have $[\alpha]_D = 30°$, and are, apparently, not dissociated. None of the tartrates which the author has examined are further dissociated in alcohol than is expressed by the specific rotatory power $[\alpha]_D = 18°$.

<div align="right">A. G. B.</div>

Molecular Rotatory Polarisation. By G. WYROUBOFF (*Ann. Chim. Phys.*, [7], **1**, 5—90; compare Abstr., 1893, ii, 106).—The rotatory polarisation of substances in the liquid, dissolved, or gaseous state is characterised as molecular, in contradistinction to the optical activity of solid substances, like quartz, which disappears on destruction of the crystalline edifice by fusion or solution. The supposition of a connection between enantiomorphous hemihedrism and circular polarisation is unjustifiable, so large a number of exceptional cases being known; thus, the enantiomorphous sodium strontium arsenite, and nitrates of lead and barium do not circularly polarise either in the crystalline or liquid state, whilst on the other hand very few optically active substances crystallise in enantiomorphous forms. The only relation which can at present be enunciated is, that optical antipodes exist of those substances which are optically active and show non-superposable hemihedrism. By varying the conditions of crystallisation of many alkaloïd salts, either right- or left-handed crystals may be obtained, although, of course, the specific rotation remains unchanged in magnitude and sign.

The author gives the name of crystalline particles to the aggregates of chemical molecules which he supposes to persist when a crystalline substance is dissolved, fused, or volatilised; he quotes a number of facts in support of this view, and has verified the old observation of Frankenheim that the red and yellow modifications of mercuric iodide can be volatilised without change of colour; the vapour of the red modification is therefore not the same as that of the yellow (compare, however, Berthelot, this vol. ii, 94).

The author defines two substances as optically isomeric when their optic axial angles do not differ by more than $10°$; he then determines the connection between the specific rotations of substances in solution and the degree of their isomorphism.

Substances which are geometrically and optically isomorphous have the same specific rotatory powers. Quinidine crystallises with 1 mol. of the alcohols of the ethylic series; the compounds with methylic and ethylic alcohol are geometrically and optically isomorphous and have the same specific rotation. The rotation is calculated on the crystalline substance, since the crystalline particles which exist in the solution have the composition of the crystals. The same is true of the following sets of substances. Cinchonine hydrobromide with $1H_2O$ and $\frac{1}{2}C_2H_6O$; cinchonidine hydrobromide with $\frac{2}{3}H_2O$, MeOH, and $\frac{1}{3}H_2O + \frac{1}{4}EtOH$; cinchonidine hydriodide with $\frac{2}{3}H_2O$ and MeOH; cinchonidine combined with HCl + MeOH and HBr + MeOH; the hydrates with $5H_2O$ of strychnine sulphate and selenate; the hydrates with $6H_2O$ of strychnine sulphate and selenate; strychnine sulphate and selenate with EtOH; the salts of cinchonidine with HBr + MeOH, HBr + $\frac{1}{3}H_2O + \frac{1}{4}EtOH$, HBr + $\frac{2}{3}H_2O$, and HCl + MeOH.

The author has also examined fully the crystallographic and rotatory properties of two other large groups of salts of the alkaloïds. The first group consists of those sets of substances which are geometrically but not optically isomorphous, whilst in the second group are placed those sets of salts which, although isomorphous among themselves, are not comparable in solution since they form different com-

pounds with the solvent; they may also dissolve without decomposition in one solvent but be partly decomposed on dissolving in another. No constancy of specific rotation was found in these cases.

W. J. P.

Electrolytic Dissociation and Optical Rotatory Power. By G. CARRARA (*Gazzetta*, **23**, ii, 587—595).—The author has determined the specific rotation of nicotine in aqueous solutions of its hydrobromide, nitrate, and propionate; the value obtained in 8—9 per cent. solutions is $+12\cdot17°$ to $12\cdot58°$. Nernst's law respecting optical activity and electrolytic dissociation is thus confirmed.

W. J. P.

Alternate Current Electrolysis. By J. HOPKINSON, E. WILSON, and F. LYDALL (*Proc. Roy. Soc.*, **54**, 407—417).—The paper contains the results of a number of experiments, the object of which was to determine (i) the dissipation of energy due to *electrolytic hysteresis*, and (ii) the quantity of an ion per square centimetre of an electrode, necessary to change the properties of the electrode to that of the ion during alternate current electrolysis. The experiments were carried out by passing an alternating current through an ordinary non-inductive resistance and through an electrolyte, and then measuring the differences of potential at the extremities of these two resistances at different phases of the current. Curves of current and potential differences with different frequency are given, as well as curves showing the dissipation of energy per cycle. As a result of the experiments, it was found that with platinum electrodes of 150 sq. cm. area, the ion being hydrogen, the maximum electromotive force due to polarisation was reached when $\frac{1}{10}$th of coulomb had passed through the cell, that is, when $0\cdot00001$ gram of hydrogen had been liberated. It hence appears that $0\cdot00000007$ gram of hydrogen is sufficient to polarise 1 sq. cm. of platinum. Assuming the density of the hydrogen to be comparable with that of liquids, the thickness of the film of hydrogen necessary is of the same order as this number—$0\cdot00000007$ cm.— a number comparable with the distance between the molecules.

L. M. J.

Minimium Electromotive Force required for the Electrolysis of Salts of the Alkalis. By C. NOURRISSON (*Compt. rend.*, **118**, 189—192).—The author has observed and calculated the E.M.F. required to electrolyse a number of salts of the alkali metals. His results, given in volts, are contained in the following table.

	Cl.	Br.	I.	SO₄.	NO₃.	ClO₃.
Potassium.............	1·97	1·74	1·15	2·40	2·32	2·45
Sodium	2·10	1·71	1·19	2·40	2·36	2·42
Lithium	2·01	—	—	2·43	2·45	—
Calcium	1·95	1·71	1·16	—	2·28	—
Barium	1·94	1·72	1·17	—	2·37	2·48
Ammonium	1·83	1·46	—	2·29	—	—
Calculated values	2·02	1·75	1·16	2·15	2·07	2·07

The solutions compared contained the same number of equivalents

per unit volume. It is pointed out that the minimum E.M.F. required for the electrolysis of salts of the alkali metals in aqueous solution is constant for salts of the same acid.   H. C.

Fusibility of Mixtures of Isomorphous Salts. By H. LE CHATELIER (*Compt. rend.*, **118**, 350—352).—The author regards all compounds as isomorphous which will crystallise together in proportions that vary continuously. The following table shows the melting points of saline mixtures, the composition of which is defined by the ratio of the total number of molecules in the mixture to the number of molecules of that salt which is mentioned second.

K_2CO_3 and Na_2CO_3	0·0	0·20	0·38	0·55	0·65	0·79	1·0	
	t. 860	770	715	690	700	740	820°	
Na_2SO_4 and K_2SO_4	0·0	0·11	0·14	0·20	0·33	0·50	0·75	1·0
	t. 860	830	825	815	830	855	940	1045°
K_2CrO_4 and K_2SO_4	0·0	0·15	0·33	0·50	0·66	1·0		
	t. 940	950	960	985	1000	1045°		
Na_2SO_4 and Na_2CO_3	0·0	0·33	0·50	0·67	0·78	1·0		
	t. 860	810	800	790	795	820°		
K_2CO_3 and K_2SO_4	0·0	0·33	0·40	0·50	0·67	0·75	1·0	
	t. 860	880	900	920	960	980	1045°	
NaCl and KCl	0·0	0·42	0·45	0·50	0·74	1·0		
	t. 780	660	650	640	690	740°		
KCl and KI	0·0	0·17	0·33	0·50	0·67	0·80	1·0	
	t. 640	610	590	580	630	680	740°	

C. H. B.

Variation of Molecular Surface Energy and Temperature. By W. RAMSAY and J. SHIELDS (*Phil. Trans.*, **184**, 647—673; compare Trans, 1893, 1089).—In this paper, the authors give the experimental details of the method which they used later for determining the molecular weights of liquids from the variation of their surface tension with the temperature. The equation which expresses this variation accurately is $\gamma s = \kappa\tau - \kappa d (1 - 10^{-\lambda\tau})$, where γ is the surface tension, s the surface, τ the temperature measured downwards from the critical temperature, d a constant difference of temperature (about 6°), and κ and λ constants. The factor $1 - 10^{-\lambda\tau}$ practically vanishes when τ is greater than 30°.

The liquids examined were ether, methylic formate, ethylic acetate, carbon tetrachloride, benzene, chlorobenzene, acetic acid, methylic alcohol, and ethylic alcohol, measurements being made as low as $-90°$ when possible. The value of κ varies from 2·04 to 2·22 for the different substances, except the alcohols, which do not come under the above formula at all.

There is no angle of contact between liquid and glass when the liquid surface is in contact with its own vapour. Ordinary measurements of capillarity give inconstant results on account of the surface tension of the liquid itself not being measured, but rather the surface tension of a solution of air in the surface film of the liquid.

The results are given in tabular and curve form.   J. W.

Combination of Sulphuric Acid with Water in the Presence of Acetic Acid. By H. C. JONES (*Amer. Chem. J.*, **16**, 1—19).—

The lowering of the freezing point of acetic acid by mixtures of sulphuric acid and water was determined and compared with the lowering produced when sulphuric acid alone or water alone was added to the acid. Evidence was thus obtained of the existence of the two hydrates, H_2SO_4,H_2O and $H_2SO_4,2H_2O$, in acetic acid solution, but the results do not indicate the existence of any hydrates containing a larger quantity of water, even when as much as 37 equivalents of water are present to one of sulphuric acid. These hydrates are somewhat unstable in the acetic acid when their solutions are very dilute, and when the excess of water present is not very great. They can be regarded as dissociated under these conditions by the acetic acid into sulphuric acid and water.

Mixtures of ethylic alcohol and water were examined in the same way, but without obtaining any evidence of the existence of compounds of the two. In the case of dry sodium acetate and water, which were also examined, some combination appears to take place, but definite results were not obtained.   H. C.

Diminished Solubility. By F. W. KÜSTER (*Ber.*, **27**, 324—328). —Nernst has shown that the solubility of one liquid in another with which it is partly miscible, is, when foreign substances are dissolved in it, diminished according to the same laws as regulate the diminution of its vapour pressure when the second liquid is not present. The experimental confirmation has been somewhat difficult to execute in a general manner on account of the limited choice of partially miscible liquids. The author has used phenol and a saturated aqueous solution of sodium chloride, and has obtained good results with these liquids. The constant $k = \dfrac{L_0 - L}{L} \cdot \dfrac{g_l}{M_l} \cdot \dfrac{M_s}{g_s} \cdot \dfrac{V}{V_0}$, has a mean value of 1·125, L_0 and L being the solubilities in water of pure phenol and of phenol containing a foreign substance, respectively, g_l and g_s the weights of phenol and of the foreign substance, M_l and M_s, their molecular weights, and V_0 and V, the volumes of phenol before and after addition of the foreign substance (compare next Abstract).   J. W.

Titration Method of Determining Molecular Weights in Solutions. By F. W. KÜSTER (*Ber.*, **27**, 328—331; compare preceding Abstract).—Two separating funnels (100 c.c. capacity) are each charged with 25 c.c. of an aqueous solution saturated at the laboratory temperature both with sodium chloride and phenol, and also with 10 c.c. of phenol saturated by contact with a concentrated aqueous solution of sodium chloride. Into one of the funnels, a weighed quantity of the substance whose molecular weight is to be determined, is introduced. This substance must be soluble in phenol and very sparingly soluble in water. Both funnels are then shaken up for two minutes, care being taken not to heat the liquids by contact with the hand, after which they are allowed to settle for half an hour. A wad of cotton-wool is now inserted into the tube of each funnel, 1 c.c. of the liquid permitted to escape, and the rest of the filtered aqueous layer collected in a small well-corked flask. The phenol in

the aqueous solution is estimated by titration with bromine (*J. prakt. Chem.*, [2], **17**, 390), 10 c.c. of the solution being introduced into stoppered bottles along with 25 c.c. of bromide-bromate solution and 10 c.c. of 10 per cent. hydrochloric acid. After half an hour, 10 c.c. of potassium iodide solution (42 g. per litre) is added, and the solution, after 15 minutes, titrated with N/20 thiosulphate solution.

The bromide-bromate solution is made by diluting the salts produced from 100 grams of sodium hydroxide and excess of bromine, first to 1 litre, and immediately before use to one-tenth of this strength.

The molecular weight of the foreign substance is calculated from the formula

$$M_s = 1\cdot125 \; g_s \frac{94}{10} \; \cdot \; \frac{L}{L_o - L},$$

where the letters have the same signification as in the preceding abstract.

For benzene, the molecular weight as thus determined varied from 74·7 to 80·1 (theory = 78); for chloroform from 95·9 to 121·0 (theory = 119·5); for vinyl tribromide from 257·5 to 294 (theory = 267).   J. W.

The Volume Theory of Crystalline Substances. By W. MUTHMANN (*Zeit. Kryst. Min.*, **22**, 497—551).—The molecular volume of crystalline substances is, as is well-known, not altogether an additive property; the molecular volume cannot be accurately calculated from the atomic volumes of the elements concerned, if these are deduced from the densities of the solid elements. A number of instances, chosen from amongst metallic salts, are quoted, showing the very inaccurate results obtained by the application of Kopp's law.

Five out of the seven different known crystalline modifications of sulphur have molecular volumes varying from 14·98 to 17·1; similarly this constant varies from 16·43 to 18·43 for the three forms of crystalline selenium. The crystalline form of the substance must consequently be taken into account in any investigation of the molecular volume of solid substances. The author considers that in polymorphous substances the chemical molecules consist of the same numbers of atoms; most probably the different molecular volumes of the various modifications are conditioned by the different distances between the chemical molecules in the physical molecules, by the different distances between the physical molecules in the crystal, and by the different numbers of chemical molecules composing the physical ones.

If two substances are strictly isomorphous, that is, if they possess similar crystalline forms, and give mixed crystals—all of whose properties are proportional to the quantity of each constituent present—it may be assumed that the weights of the elements of the crystalline masonry of each are proportional to the equivalent weights of the substances concerned. This assumption, however, can only be made in cases of perfect isomorphism, and would not necessarily hold between potassium chloride and sodium chloride, the former being

asymetrically hemihedral and cubic, and the latter being holohedrally cubic.

The relative size of the elements of the crystalline masonry can now be calculated. Let S_a and S_b be the specific gravities of two isomorphous substances a and b of molecular weight W_a and W_b respectively; let also the volumes of the elements of the crystalline structure be V_a and V_b, and the corresponding molecular volumes be M_a and M_b; then

$$\frac{V_a}{V_b} = \frac{W_a \, S_b}{S_a \, W_b} = \frac{M_a}{M_b}.$$

Now, the element of crystalline masonry, according to the theory of crystal structure developed by Bravais and Sohncke, is a parallelopipedon; in the tetragonal system, this parallelopipedon has a square base and the ratio of the length of the side to the height is indicated by the ratio $a : c$, of the lengths of the crystallographic axes. Let the heights of the parallelopipeda in the two substances be χ_a and χ_b, and the lengths of the sides of the basal square be w_a and w_b respectively. Then a very simple calculation shows that

$$\frac{\chi_a}{\chi_b} = \sqrt[3]{\frac{c_b \, a_a \, M_a}{a_b \, c_a \, M_b}} \text{ and } \frac{w_a}{w_b} = \sqrt[3]{\frac{a_b^2 \, c_a^i \, M_a}{c_b^i \, a_a^2 \, M_b}},$$

where $a_a : c_a$ and $a_b : c_b$ are the crystallographic axial ratios for the substances a and b respectively. Putting $a : c = 1 : m$ for any substance.

$$\chi : w = \sqrt[3]{\frac{M}{m}} : \sqrt[3]{M m^2}.$$

This ratio of the dimensions of the crystallographic element the author terms the "topical" axial ratio ($\tau \acute{o} \pi o s$, space); for a crystalline system of lower symmetry than the tetragonal, the topical axial ratio contains three terms, $\chi : \phi : w$, representing the dimensions of the elementary parallelopipedon in the three crystallographic directions a, b, and c. The topical axial ratio consequently measures the distances between the elements of crystalline structure in the three directions a, b, and c.

The author has calculated the topical axial ratios for the tetragonal ammonium and potassium arsenates and phosphates as follows.

	ϕ.	:	χ.	:	w.
KH_2PO_4............	3·1419	:	4·4432	:	2·9503
KH_2AsO_4	3·2232	:	4·5583	:	3·0235
$NH_4H_2PO_4$.........	3·1698	:	4·4827	:	3·1934
$NH_4H_2AsO_4$	3·2491	:	4·5949	:	3·2606

For purposes of comparison, χ is calculated as the diagonal of the square of side ϕ; consequently $\chi = \phi\sqrt{2}$. By comparison and subtraction of these numbers it is seen (1) That the distances of the molecules from each other in ammonium or potassium phosphate are increased by the same ratio in each direction when arsenic is substituted for the phosphorus; (2) That the increase in this distance is approximately the same in both ammonium and potassium salts; (3) That

on substituting arsenic for phosphorus in potassium or ammonium phosphate, the centres of gravity of the crystal molecules move further apart and to an equal extent in all directions; (4) That on replacing potassium by ammonium in potassium phosphate or arsenate, the distances between the centres of gravity of the molecules become greater, the maximum increase occurring in the direction of the principal axis c, and the minimum in the direction of the secondary axis a. From these conclusions, the author deduces that the crystalline molecules of these phosphates consist of eight chemical molecules.

The author has obtained most perfect crystals of the orthorhombic permanganates of the alkali metals by allowing hot concentrated solutions of the salts to cool in a water-jacketed vessel containing 25 litres of hot water; the cooling occupied five days. The following results were obtained.

Salt.	a : b : c	χ : ϕ : ω	Sp. gr. at 9—10°.
$KMnO_4$....	0·79724 : 1 : 0·64908	3·8554 : 4·836 : 3·139	2·7035
NH_4MnO_4..	0·8164 : 1 : 0·6584	3·9767 : 4·8711 : 3·2071	2·2076
$RbMnO_4$...	0·83110 : 1 : 0·66616	4·0322 : 4·8517 : 3·2312	3·2248
$CsMnO_4$ ...	0·86831 : 1 : 0·68525	4·2555 : 4·9009 : 3·3584	3·5974

The molecular volumes of the four salts are 58·526, 62·126, 63·228, and 70·042 respectively.

The relations observed by Tutton (Trans., 1893, 337) between the crystalline forms of the double sulphates containing potassium, rubidium, and cæsium, are found still to hold between those of the permanganates. The differences between the axial ratios of the potassium and rubidium salts are the same as between those of the rubidium and cæsium salts. The difference between the molecular volumes of cæsium and rubidium permanganates is greater than the corresponding difference for the potassium and rubidium salts; this, the author shows, is always true for isomorphous salts of these three metals. The author concludes, further, that in an isomorphous series an increase in molecular weight is accompanied by an increase in molecular volume, if the elements which differ in the various members belong to the same group in the periodic system; if the latter is not the case, no relation is found between the molecular volumes and the molecular weights.

Very similar conclusions are drawn from the topical axial ratios of the permanganates as are deduced above from the phosphates and arsenates. The topical axial ratio of potassium perchlorate is also considered in its relation to that of the permanganate, and a comparison of Bravais' space lattice theory and Sohncke's point system theory of crystalline structure is made. W. J. P.

System of the Haloid Salts according to the Theory of Chemical Forms. By F. FLAVITZKY (*J. Russ. Chem. Soc.*, **25,**

223—262).—The author, feeling the insufficiency of the ordinary
theory of valency to account for many types of the inorganic com-
pounds, has developed a theory of chemical forms which is intended
to embrace not only the common anhydrous compounds, but also the
hydrated acids, salts, &c. To take an example, the forms derived
from the theory for the elements of the seventh periodic group are
as follows.

Fundamental forms—$R(OH)_7$, $RH(OH)_6$, $RH_2(OH)_5$, $RH_3(OH)_4$,
$RH_4(OH)_3$, $RH_6(OH)$, RH_7.

From these are derived the primary anhydrides.

   (*a.*) Saturated, $R(OH)_5O$, $RH(OH)_4O$, $RH_2(OH)_3O$, $RH_3(OH)_2O$,
      $RH_4(OH)O$, RH_5O.
   (*b.*) Unsaturated, $[R(OH)_5]''$, $[RH(OH)_4]''$, $[RH_2(OH)_3]''$,
      $[RH_3(OH)_2]''$, $[RH_4(OH)]''$, $[RH_5]''$.

The secondary anhydrides are

   (*a.*) $R(OH)_3O_2$, $RH(OH)_2O_2$, $RH_2(OH)O_2$, RH_3O_2.
   (*b.*) $[R(OH)_3O]''$, $[RH(OH)_2O]''$, $[RH_2(OH)O]''$, $[RH_3O]''$.
   (*c.*) $[R(OH)_3]^{iv}$, $[RH(OH)_2]^{iv}$, $[RH_2(OH)]^{iv}$, $[RH_3]^{iv}$.

The tertiary anhydrides are

   (*a.*) $R(OH)O_3$, RHO_3.
   (*b.*) $[R(OH)O]''$, $[RHO_2]''$.
   (*c.*) $[R(OH)O]^{iv}$, $[RHO]^{iv}$.
   (*d.*) $[R(OH)]^{vi}$, $[RH]^{vi}$.

In this paper, the author discusses the haloid salts, and refers them
to the various forms given above; thus the salt $LiClO_4,3H_2O =$
$Cl(LiH_6)O_7$ corresponds with the first of the fundamental forms, the
acid $HClO_4,2H_2O = Cl(OH)_5O$ to the first of the primary saturated
anhydrides, the salt $LiI,3H_2O = I(LiH_3)(OH)_3$ to the fifth of the
fundamental forms, the salt $NaI,2H_2O = I(NaH_3)(OH)O$ to the fifth
of the primary saturated anhydrides, &c.   J. W.

Stereochemistry. By SEELIG (*J. pr. Chem.*, [2], **49**, 134—136).
—Remarks on the utility of stereochemical theories.   A. G. B.

**Decomposition of Solutions by Contact with finely sub-
divided Silica, Titanic acid, Stannic Oxide, Alumina, Ferric
Oxide, Magnesium Carbonate, Calcium Carbonate, or Barium
Sulphate.** By G. GORE (*Chem. News*, **69**, 22—24, 33, 43—46).—To
ascertain the effect produced by silica, various solutions of known
composition and strength were shaken, in quantities of 25 c.c., with
50 grains of suitably prepared pure precipitated silica, and allowed
to settle during 16 to 20 hours; the supernatant liquids being
then analysed. The following solutions lost in strength :—*Solutions
of less than* 1 *per cent.*, hydrochloric acid, potassium and sodium
chlorides, carbonates and cyanides, ammonium carbonate and iodine;
1, 5, *and* 10 *per cent. solutions of* hydrochloric acid, zinc, magnesium,
calcium and ammonium chlorides, potassium and sodium carbonates

and cyanides, ammonium hydroxide and carbonate, and potassium bromide ; 5 *and* 10 *per cent. solutions* of nitric acid, potassium iodide and sodium bromide ; 1 *and* 10 *per cent.* cadmium, strontium, and sodium chlorides, and potassium hydrogen sulphate ; 1 *and* 5 *per cent.* potassium chloride. 10 *per cent. solutions*, acids—hydrobromic, hydriodic, chloric, perchloric, iodic, phosphoric, pyrophosphoric, tartaric and citric ; chlorides—cobalt, barium, lithium, rubidium ; sulphates— copper, iron, ammonium and rubidium ; potassium nitrate, sodium and rubidium iodides, ammonium bromide, and trimethylamine : 5 *per cent.* succinic acid and disodium hydrogen phosphate. The following solutions gained in strength :—1 per cent. pyrophosphoric acid, 1 and 10 per cent. copper chloride, 10 per cent. cobalt, manganese, cadmium, zinc magnesium, sodium and potassium sulphates, and manganese chloride ; and 5 per cent. potassium chlorate and iodate. The following solutions were apparently unaffected :—1 and 10 per cent. sulphuric acid ; 1 and 5 per cent. lithium chloride, sodium iodide, and ammonium bromide ; 10 per cent. chromic acid, nickel chloride and sulphate, potassium chloride and hydrogen sulphate, iron chloride, and rubidium bromide ; 5 per cent. oxalic acid, cadmium, strontium and sodium chlorides, and potassium nitrate ; 1 per cent. nitric, perchloric and phosphoric acids, zinc sulphate, potassium iodide and sodium bromide, 3 per cent. borax and $\frac{1}{4}$ per cent. potassium, and $\frac{1}{10}$ per cent. sodium chloride.

Increasing the amount of silica also increases the effect; the character of the solvent alters the effect, which, however, is not much changed by variations in temperature. Shaking with, is found more effective than percolation through, silica. The action is complete within four hours, and with acid and neutral salts, as is shown, is not regular; but with alkaline salts the amount abstracted from solution is generally greater, but the proportion less, the stronger the solution. Salts in admixture interfere with one another. With pulverised titanic acid, 1 per cent. potassium, sodium, and ammonium carbonates, and ammonium hydroxide lost in strength, but to a less extent than with silica ; 1 per cent. potassium cyanide was not affected. Neither stannic oxide nor calcium carbonate was effective in four hours, whilst alumina, ferric oxide, magnesium carbonate, and barium sulphate were less active than silica. Barium sulphate formed in the solution was found more active than the previously prepared precipitate. Mixed powders, such as silica and alumina, silica and barium sulphate, like the mixed salts, interfere with one another's action. The wetting of the powder is in all cases accompanied by an evolution of air bubbles. The results show that the abstraction of dissolved substances from solution by finely-divided solids depends not only on the character and quality of the solid, but also on the strength and composition of the solution, and on the nature of the solvent employed. *D. A. L.*

A New Thermometer for High Temperatures. By E. C. C. BALY and J. C. CHORLEY (*Ber.*, **27**, 470—471).—The instrument is made like an ordinary thermometer, but of " resistance "-glass, which will stand a red-heat ; it is filled with a liquid alloy of sodium and

potassium, and is graduated from 200 to 650°.   The space above the
alloy is filled with nitrogen at such a pressure that, when the bulb is
red hot, and consequently somewhat soft, the pressure inside is equal
to that of the atmosphere.   Only the bulb and 9 cm. of the stem are
exposed to the temperature to be measured, but no correction is
needed, for the stem is graduated in equal divisions, whereas the co-
efficient of expansion of the alloy increases with the temperature.
The glass of the bulb is attacked by the alloy and turned brown, but
this occurs at the time of filling the bulb, and the coating then formed
upon the surface of the glass protects the latter from subsequent
action of the alloy.   C. F. B.

Oven for the Prevention of the Explosion of Sealed Tubes.
By C. ULLMANN (*Ber.*, **27**, 379—382).—In order to prevent, or in
any case minimise, the risk of explosion of sealed tubes, the author
introduces the sealed tubes into a strong steel tube, tested to 600
atmospheres, and containing 40—70 c.c. of ether, light petroleum, or
other suitable liquid which does not attack glass at a high tempera-
ture.   The steel tube is closed by means of a screwed cap and leaden
washer, and heated as usual in a stove to the requisite temperature.
The pressure caused by the vapour tension of the liquid in the steel
tube more or less counteracts the pressure inside the glass tube, and
thus reduces the risk of explosion to a minimum.   In cases where the
glass tube contains acid, pieces of lime are introduced into the steel
tube to prevent corrosion of the latter in case of failure of the glass.
                                                                      H. G. C.

Inorganic Chemistry.

Preparation of Hydrogen Peroxide. By P. Shiloff (*J. Russ. Chem. Soc.*, **25**, 293—294).—Sodium carbonate is added to the commercial 3 per cent. aqueous solution of hydrogen peroxide, until the reaction is distinctly alkaline. The solution is then filtered, and shaken up for 3 to 5 minutes with 10—12 times its volume of ether, which extracts about half of the hydrogen peroxide originally present, and leaves behind most of the impurities. The ethereal layer is separated and reduced to 0·01—0·0025 of its original volume on the water bath. The remainder of the ether is removed in a bell-jar by solid paraffin. The loss of hydrogen peroxide during the evaporation of the ether is only 7—10 per cent.

Operating in this way, the author obtained (*a*) a colourless solution with distinctly acid reaction, and sp. gr. 1·1756, which contained 54 grams of anhydrous hydrogen peroxide in 100 c.c.; (*b*) a thick, transparent, slightly yellow, acid liquid, of sp. gr. 1·2475, which contained 79·6 grams of hydrogen peroxide in 100 c.c. J. W.

Source of Atmospheric Hydrogen Peroxide. By A. Bach (*Ber.*, **27**, 340—344).—The author has been led to the conclusion

that carbonic acid in sunlight undergoes decomposition into percarbonic acid and the elements of formaldehyde, according to the equation

$$3H_2CO_3 = 2H_2CO_4 + \boxed{C + H_2O}$$
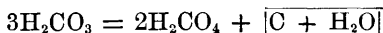
The percarbonic acid may afterwards decompose into carbonic anhydride and hydrogen peroxide, $H_2CO_4 = CO_2 + H_2O_2$. To these reactions, he attributes the presence of hydrogen peroxide in the atmosphere.

A cold, saturated, and filtered solution of uranium acetate, containing 1 per cent. of freshly-distilled diethylaniline, gives a violet coloration when exposed to the simultaneous action of carbonic anhydride and strong sunlight, although it is unaffected in this sense by either of these agents separately. This must be due to the formation of formaldehyde and of a compound (percarbonic acid), which will oxidise the leuco-base produced by the action of the formaldehyde on the diethylaniline.　　　　　　　　　　　　　　　　J. W.

Decomposition of Hydroxylamine by Sodium Hydroxide.

By S. KOLOTOFF (*J. Russ. Chem. Soc.*, **25**, 295—296).—An aqueous solution containing 6 grams of hydroxylamine sulphate and 12 grams of sodium hydroxide in 90 c.c. was allowed to remain for several days at the ordinary temperature. It was then found that all the hydroxylamine had decomposed in the sense of the following equations

$$3NH_3O = NH_3 + N_2 + 3H_2O,$$
$$4NH_3O = 2NH_3 + N_2O + 3H_2O,$$
$$3NH_3O = 2NH_3 + HNO_2 + H_2O.$$
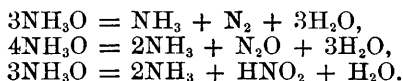
Hydroxylamine sulphate contains 17·07 per cent. of nitrogen, which was found to be distributed amongst the products of decomposition as follows.

Nitrogen in ammonia............	7·12	per cent.
,,　　　 sodium nitrite.......	0·39	,,
,,　　　 nitrous oxide........	2·22	,,
Free nitrogen	6·68	,,
	16·41	,,

When hydroxylamine is oxidised by the calculated quantity of sodium hypobromite in alkaline solution, and by potassium permanganate in acid solution, hyponitrous acid is formed in small quantities, probably from the action of the nitrous acid primarily obtained on the excess of hydroxylamine.　　　　　　　　　　　　J. W.

Compounds of Hydroxylamine with Metallic Salts.

By W. FELDT (*Ber.*, **27**, 401—406).—The following compounds have been prepared. $CoCl_2,2NH_3O$ is obtained by heating cobalt chloride with hydroxylamine hydrochloride and a little free hydroxylamine in alcoholic solution, on the water bath, in an atmosphere of hydrogen. It forms pink crystals, which decompose in the air, more rapidly when exposed to light, with formation of nitrous acid, but may be

preserved in closed vessels; when heated, it decomposes suddenly, with formation of vapours of ammonia and ammonium chloride.

$CoSO_4,NH_3O + 2H_2O$ is prepared in a similar manner, aqueous solutions being, however, employed. It is insoluble in cold water, but dissolves in hot water; oxidation, accompanied by the separation of a brown product, however, soon occurs in the solution. The salt is more stable than the chloride, and may be preserved for some time in the air.

$CoOCl,2NH_3O$ is an unstable insoluble substance, obtained by passing oxygen, under an extra pressure of $\frac{1}{4}$ atmosphere, into an alcoholic solution of cobalt chloride and free hydroxylamine. When this compound is suspended in cooled alcohol and treated with alcoholic hydrochloric acid, the salt, $CoCl_3,6NH_3O$, is formed as a yellow, crystalline precipitate; the latter dissolves in acidified water, crystallises in the monosymmetric system, and is dissolved without decomposition by concentrated sulphuric acid; it corresponds in composition with luteocobalt chloride. When ammonium oxalate is added to its aqueous solution, a precipitate, consisting of yellow needles of the composition $Co_2(C_2O_4)_3,12NH_3O$, is formed.

$MnCl_2,2NH_3O$ is a very stable substance, and only decomposes at 150—160°. $MnSO_4,NH_3O + 2H_2O$ is a white powder, insoluble in water. Attempts to obtain additive products with salts of copper and mercury proved unsuccessful.   A. H.

Diamidophosphoric acid and Diamidotrihydroxyphosphoric acid. By H. N. STOKES (*Ber.*, **27**, 565—567).—*Diamido-ortho-phosphoric acid* is obtained in a similar manner to the monamido-acid (Abstr., 1893, i, 316), by treating the dichloride of phenylphosphoric acid with aqueous ammonia, and hydrolysing the product. It is a crystalline substance, which is stable when dry, and is readily decomposed by acids, but is scarcely attacked by boiling aqueous alkalis. Nitrous acid converts it, first, into monamidophosphoric acid, and then into orthophosphoric acid itself. With the alkali metals and alkaline-earth metals, it forms salts, which are remarkably soluble in water, and do not crystallise. The *silver* salt, $PO(NH_2)_2\cdot OAg$, crystallises well; a second silver salt is also known, which has the composition $P(NH)(NH_2)(OAg)_2$, and is amorphous. When this substance is boiled with water or allowed to remain for two days under cold water, it is converted into the primary salt, and a splendid dark red salt, which probably has the composition $P(NAg)(NHAg)(OAg)_2$, detonates slightly when heated, and is decomposed by concentrated sulphuric acid with production of flame.

When the first-mentioned salt is covered with aqueous potash of moderate concentration, it swells up, forming a stiff, colourless jelly, which, on dilution with water, yields a remarkably viscid solution; the jelly probably contains the salt $P(NH_2)_2(OK)_2\cdot OAg$. After some hours, colourless needles having the composition $P(NH_2)_2(OAg)_2\cdot OK$, are deposited from this jelly, whilst the mother liquor contains potassium diamidophosphate and free alkali. If these needles are washed with water, decomposition takes place, and a yellow-coloured substance of the formula $P(NH_2)_2(OAg)_3$ is free

formed, which again, on treatment with hot water, is converted into free acid, and a reddish-brown substance containing 4 atoms of silver, $P(NHAg)_2(OAg)_2 \cdot OH$; this is finally converted into the red salt, described above, by boiling with water.

If the viscid solution, already referred to, be further diluted with water, a clear, wine-red solution is obtained, from which carbonic anhydride precipitates an amorphous substance, which in appearance resembles freshly precipitated ferric hydroxide, and has the composition $P(NHAg)_2(OAg)_2 \cdot OH$ (see above). It explodes feebly when heated, and on boiling with water is converted, with loss of the elements of water, into the red salt.

If the jelly is so far diluted with water that it only contains 2—3 per cent. of alkali, a brown, amorphous salt, resembling silver oxide, is deposited, which has the formula $P(NHAg)_2(OAg)_3$. In the dry state, it explodes violently when rubbed, heated, or brought into contact with concentrated sulphuric acid.

Diamidophosphoric acid appears, therefore, to be capable of combining with 1 mol. of water or base to form the diamide of a pentabasic phosphoric acid, in which the two amido-groups play the part of hydroxyl-groups, 1 atom of hydrogen in each being replaceable by metals. A. H.

An Application of Sodium Silicate. By G. GEISENHEIMER (*Compt. rend.*, 118, 192—194).—In order to ensure the complete bleaching of linen, it is customary to increase the causticity of the ley, and to prolong the time of boiling, with the result that the fabric is often injured. The production of yellowish or brownish patches is usually attributed to impurities in the chemicals used, but is chiefly due to the presence in the water of calcium and magnesium salts, which are precipitated on the fabric, and act as mordants, fixing the yellowish colouring matter of the ley. This injurious effect can be prevented by adding to the water a mixture of sodium carbonate and silicate; this precipitates calcium and magnesium silicates in a flocculent form, which settles rapidly, does not adhere to the fabric, and becomes granular and pulverulent on boiling with water. Thus purified, only a very small quantity of caustic alkali is necessary, the greater part of the saponification being effected by means of the less injurious alkali carbonate.

A convenient form in which to use sodium silicate is to add from 10 to 20 per cent. of anhydrous sodium carbonate to a saturated solution of sodium silicate. The product is easily handled, and remains completely soluble in water. Further, the quantity necessary for a particular water can readily be calculated. C. H. B.

Reproduction of the Diamond. By H. MOISSAN (*Compt. rend.*, 118, 320—326).—Attempts to employ bismuth, in place of iron or silver, in the preparation of carbon under high pressure (Abstr., 1893, ii, 275) were unsuccessful, the fused mass exploding violently when plunged into water. Further experiments with iron have confirmed the previous results (*loc. cit.*), but the yield of diamonds of sp. gr. between 3·0 and 3·5 is extremely small. Experiments with larger

quantities of iron gave no better results, seemingly because of the difficulty of saturating the metal with carbon. In order to obtain more rapid cooling, the fused iron saturated with carbon was poured into a cavity in a mass of iron filings. In this way small, rounded diamonds were obtained, which rarely showed any crystalline appearance, and they almost always enclosed black specks. They have a sp. gr. of 3·5, scratch rubies, and burn readily in oxygen.

The molten iron cannot be cooled in tin, because of the readiness with which the two metals unite, but it can be cooled by pouring it into a bath of melted lead ; small globules of the iron rise to the surface, and are cooled and solidified before they reach it. When these solidified globules are treated with acids in the usual way, the yield of diamonds is somewhat better, and they are very limpid, have no black enclosures, and some show distinct crystallisation. They also show, in many cases, parallel striæ, and impressions of cubes similar to those observed on certain natural diamonds. Two of the specimens broke spontaneously some time after preparation. One of the crystals showed distinctly curved faces. Some of the diamonds show smooth and brilliant surfaces, whilst others have a granular surface, such as is frequently seen on natural diamonds. Some of the crystals were found by Bouchardat to be trapezohedrons with 12 faces. With convergent polarised light, some of the crystals showed no coloration, whilst others showed feeble colours, much less intense than the colours observed with many natural crystals under similar conditions. From the appearance of the crystals, it seems probable that carbon, like iodine and arsenic, changes at the ordinary pressure, and at a sufficiently high temperature, from the solid to the gaseous state, but under a very high pressure can be liquefied, and remain in superfusion, taking a crystalline form when it solidifies.

Further experiments with silver saturated with carbon gave results similar to those previously described (*loc. cit.*), but only black diamonds were obtained.

0·0155 gram of diamonds heavier then methylene iodide gave 0·0496 gram of carbonic anhydride and 0·0025 gram of ash.

C. H. B.

Behaviour of the Liquid Alloy of Sodium and Potassium in Contact with Dry Oxygen Gas. By G. S. JOHNSON (*Chem. News*, **69**, 20).—The liquid alloy of sodium and potassium remains unaltered in dry oxygen gas at the ordinary temperature, but at a temperature below redness it kindles and burns with explosive violence.   D. A. L.

Pentahydrates of Sodium Bromide and Sodium Iodide. By I. PANFILOFF (*J. Russ. Chem. Soc.*, **25**, 272—275).—The pentahydrate of sodium iodide is obtained by cooling a solution of sodium iodide (100 grams) in water (50 c.c.) to $-14°$, the temperature rising to $-13·5°$ when the crystallisation begins. At $-10°$, it passes into the dihydrate and water.

The pentahydrate of sodium bromide crystallises slowly from a strong aqueous solution at the out-door winter temperature in Russia. It decomposes into the dihydrate and water at $-25°$.   J. W.

Hydrogel and Crystalline Hydrate of Copper Oxide. By J. M. VAN BEMMELEN (*Zeit. anorg. Chem.*, **5**, 466—483).—The colloïdal hydrate (hydrogel) is purified by repeated and rapid washing with large quantities of cold water (1 litre per gram), the mass being collected on a cloth filter after each washing, and the operation not lasting more than an hour, to avoid change of colour. The pure hydrogel is a thick, bright blue jelly, which, after pressing between porous earthenware for two hours, still contains a large quantity (20 mols.) of "water of absorption." It retains its colour under water at the ordinary temperature for several days, whether in the dark or in sunlight, but in hot water, unlike the crystalline variety, undergoes gradual modification, the colour changing to green. When, exposed at the ordinary temperature to an artificially dried atmosphere, it loses water until its vapour pressure is equal to that of the aqueous vapour in the atmosphere, and when the pressure is zero, the composition approaches the limit CuO, H_2O. This last molecule of water is only partially eliminated at $100°$; the second, although not so tenaciously attached, is more firmly combined than the others, the number of which varies, as before stated, with the pressure. With the elimination of water, the compound becomes more stable, and like the crystalline hydrate in character, whilst the ease with which the water is eliminated diminishes as time elapses; alkalis, however, facilitate the elimination. The dried substance absorbs a certain amount (4 mols.) of the water again, when exposed to a moist atmosphere, the exact amount depending, as before, on the pressure of the aqueous vapour in the atmosphere. The hydrogel is stable towards alkalis and alkali salts, but precipitates bromides and iodides, almost completely, as basic cuprous compounds; the fresher the preparation, the more vigorous the action.

The crystalline hydrate, CuO, H_2O, prepared by the slow action of dilute alkalis on various copper salts in the cold, is not affected by alkalis or by heat, and may be boiled with water without undergoing any change. The assumption of this stable form is in some way connected with the action of the alkali, as the same phenomenon is observed with beryllia and alumina.   Jn. W.

Interaction of Ferric Chloride with Potassium and Hydrogen Iodides. By K. SEUBERT and A. DORRER (*Zeit. anorg. Chem.*, **5**, 411—436).—A continuation of previous work (Abstr., 1894, ii, 140). The action with hydrogen iodide closely resembles that with potassium iodide. With molecular proportions ($FeCl_3 : HI$), the yield of iodine never approaches the theoretical, though it increases steadily with the time, from $38·2$ per cent. in 15 minutes to a maximum of $73·2$ per cent. in 58 days. With increasing proportions of hydrogen iodide, but the same concentration of ferric chloride, the yield also increases, reaching $95·4$ per cent. in 15 minutes, and a maximum of $98·9$ per cent. in 17 hours with the ratio $FeCl_3 : 5HI$, and $99·0$ and $100·8$ per cent. in 18 hours with the ratios $FeCl_3 : 10HI$ and $FeCl_3 : 15HI$ respectively. With the ratio $10FeCl_3 : HI$, and the same concentration of hydrogen iodide as in the first experiment, $73·2$ per cent. of the theoretical amount of iodine is liberated in 15 minutes,

and 98 per cent. in 25 hours; with the ratios $15FeCl_3 : HI$ and $20FeCl_3 : HI$, 97·8 and 100 per cent. respectively in 18 hours.

Continuing the experiments with potassium iodide, the yield diminishes with the concentration, and, finally, almost vanishes. Mixed in molecular proportion and at concentrations twice and four times that in the previous experiments, the yield, in about 42 hours, increases from 59·9 per cent. to 67·5 (70·3 in 143 hours) and 75·2 per cent., whilst at half the concentration it diminishes to 50·6, at one-fifth to 41·0, at one-thirtieth to 5·35, and at one-fortieth to 1·25 per cent. The effect of dilution on the influence of excess of either substance is to decrease the rate at which the yield attains the maximum, both with regard to time and to the ratios of the reacting masses.

The influence of temperature on the action is distinctly unfavourable, owing to the precipitation of ferric oxychloride, and consequent removal of iron from the sphere of action; this bye-action may, however, be eliminated by the addition of hydrochloric acid in the ratio $FeCl_3 : 3HCl$. The immediate yield (30 minutes) with the ratio $FeCl_3 : KI$ then increases from 39·9 to 79·5 per cent., but diminishes on keeping at the ordinary temperature, owing to the reabsorption of iodine, a limit being reached in 41 hours, practically identical with that attained by a similar unheated mixture, or by a mixture, in molecular proportion, of ferric chloride and hydrogen iodide of the same concentration. The same phenomenon occurs with other ratios of ferric chloride to potassium iodide.

It is thus evident that the action follows the course indicated by the usually accepted equation, $FeR_3 + MI = FeR_2 + MR + I$, only under very strictly defined and special conditions. This is to be accounted for on the hypothesis that the action is reversible in the sense expressed by the equation $FeR_2 + MR + I = FeR_3 + MI$, in which case the maximum or limiting yield in the foregoing experiments corresponds with the point of equilibrium at which the velocities of the opposing reactions are equal. That this supposition is correct is evident from the result of the interaction of various molecular proportions of iodine with a mixture of ferrous and potassium chlorides in molecular proportion; in every case, the amount of iodine remaining after 60 hours corresponds with that liberated by an equivalent mixture of ferric chloride and potassium iodide in the same time. It is only in extreme cases, therefore, that the amount of iodine corresponding with the first equation will be liberated. The reason that the full amount is liberated in the analytical processes of Topf (Abstr., 1887, 998) and Stortenbeker (Abstr., 1890, 1185) is that either the iron or the iodine is removed from the sphere of action, in the one case by the precipitation of basic ferric acetate, in the other by the distillation of hydrogen iodide.

As to the mechanism of the action, it is most improbable that the chlorine of the potassium chloride is displaced by free iodine, and another explanation must be looked for. It appears that a mixture of very dilute solutions of ferric chloride and potassium iodide exhibits, after a long time, a yellowish-brown colour, which is not destroyed by thiosulphate, and is much deeper than that of a solution of ferric chloride of corresponding strength. It seems to be due to ferric

chloriodide, $FeCl_2I$, a compound corresponding with Lenormand's chlorobromide, $FeCl_2Br$ (Abstr., 1893, ii, 377), for a mixture of neutral aqueous ferrous chloride with alcoholic iodine exhibits also a brownish-red colour, which is likewise not due to free iodine. The substance is not ferric oxychloride, $FeCl_2 \cdot OH$, for iodine is liberated on dilution with water, which could scarcely be the case if the oxychloride had been formed in accordance with the equation $FeCl_4 + I + H_2O = FeCl_2 \cdot OH + HI$. The amount of iodine liberated corresponds, too, with that contained in the chloriodide. Attempts to obtain the compound in the solid state by evaporating the solvent yielded, however, only mixtures of its proximate constituents.

If this chloriodide, then, is formed as an intermediate product, the mechanism of the whole action is clear. The chloriodide is first produced in accordance with the equation $FeCl_3 + KI = FeCl_2I + KCl$, and then decomposed, more or less completely, into ferrous chloride and free iodine, according to conditions of time, concentration, temperature, and mass. But, since the latter reaction is reversible, the chloriodide, and, probably, the chloride, are formed again until equilibrium is attained, the actual position of the point of equilibrium depending on the conditions.

There is thus no need to assume, with Carnegie (Abstr., 1889, 1113), that potassium iodide is a direct reducing agent, nor, if means be taken to remove one of the products from the sphere of action, to require more than 1 mol. of potassium iodide for each mol. of ferric chloride. Duflos' equation, $FeCl_3 + 3KI = FeI_2 + 3KCl + I$, cannot, in any case, be true, for under the least favourable conditions of mass, 60 per cent. of the iodine in the potassium iodide is liberated.

Jn. W.

Phosphochromates. By M. BLONDEL (*Compt. rend.*, **118**, 194—195). —When a highly concentrated solution of phosphoric and chromic acids, containing 8 mols. of the latter to 1 mol. of the former, is mixed with three-fourths of a molecular proportion of potassium carbonate, the salt, $3K_2O,P_2O_5,8CrO_3$, is precipitated in the form of small, short prisms. If the solution contains only 2 mols. of chromic acid, the product is $2K_2O,P_2O_5,4CrO_3,H_2O$, which crystallises in needles. If the latter solution, however, is mixed with some crystals of the first salt, the precipitate at first consists of this salt, which, however, if left in contact with the liquid, is converted into the second salt. The salt, $3K_2O,P_2O_5,8CrO_3$, is converted into the salt

$$2K_2O,P_2O_5,4CrO_3,H_2O,$$
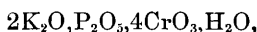
by treatment with water or a saturated solution of potassium dichromate.

C. H. B.

Phosphovanadic Acids and their Salts. By C. FRIEDHEIM (*Zeit. anorg. Chem.*, **5**, 437—465; compare Abstr., 1890, 1067).— Although the vanadates are usually regarded as strictly analogous to the phosphates, they do not correspond with them in all respects. They show, for instance, a much greater tendency to form acid salts. When sodium metaphosphate and vanadate are brought together in

solution, the phosphate is converted into trisodium orthophosphate, whilst the vanadate assumes some such form as the acid salt,

$$5Na_2O,8V_2O_5 + 39H_2O,$$
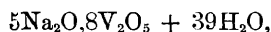
or, if potassium chloride is present, an isomorphous mixture of potassium and sodium salts of a similar character. Monosodium orthophosphate behaves in much the same manner, and potassium pyrophosphate and pyrovanadate interact in a similar way.

On the other hand, it seems that the dark, reddish-brown *purpureo-salts (loc. cit.)*, obtained from mixtures of monopotassium orthophosphate and potassium metavanadate, or of potassium metavanadate and phosphoric acid under certain somewhat indefinite conditions are isomorphous mixtures of monopotassium phosphate and vanadate Although the salts obtained in this way in rectangular plates are somewhat variable in composition, the ratio of basic to acid oxide tends towards 1 : 2, and, in some cases, reaches that figure, whilst the ratio of phosphoric to vanadic acids approaches 1 : 12. They may thus be regarded as potassium divanadate, $K_2O,2V_2O_5$, in which a portion of the vanadic oxide is isomorphously displaced by phosphoric oxide. Similar instances of isomorphous substitution of vanadium by phosphorus occur in the natural compounds eusynchite and vanadinite. Since, to form such isomorphous mixtures, potassium divanadate must be isomorphous with monopotassium orthophosphate, it would seem that the present nomenclature of the vanadates requires revision. It was incidentally observed that the pupureo-salts obtained by the addition of the proper amount of nitric acid to mixtures of potassium metavanadate and dipotassium orthophosphate were always contaminated with nitric acid, and it is possible that this may also exist in isomorphous replacement of vanadic acid, since nitrogen belongs to the same periodic group as vanadium and phosphorus.

The yellow, crystalline, *luteo-compound*, K_2O,V_2O_5,P_2O_5 *(loc. cit.)*, may be regarded either as having the constitution

$$OH·PO(OK)·O·VO_2,$$
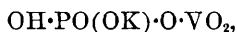
with vanadoxyl functioning as base, or as an isomorphous mixture, similar in character to the purpureo-compound. The constancy and equality of the ratio of phosphoric to vanadic oxide is not out of harmony with the latter view, for similar compounds are known in barytocalcite and zinc copper sulphate. Another luteo-compound may be regarded as a mixture having the composition $PO(OK)_2·O·VO_2 + OH·PO(OK)·O·VO_2$, analogous to sodium diphosphate. Others are still more complex.

When an excess of base is present in a mixture from which purpureo- or luteo-compounds might otherwise be expected, colourless, crystalline compounds separate, consisting of isomorphous mixtures of potassium metavanadate and monopotassium orthophosphate contaminated with dipotassium orthophosphate.   JN. W.

Mineralogical Chemistry.

Analyses of the Mineral Combustible Gases of Torre and Salsomaggiore. By D. Gibertini and A. Piccinini (*Gazzetta*, **23**, ii, 559—576).—The authors have analysed a natural gas which issues at Torre in Parma; it is accompanied by water of alkaline reaction and a small proportion of petroleum. The gas contains about 95 per cent. by volume of methane and 0·12 per cent of carbonic oxide. A gas containing 91 per cent. of methane issues at Salsomaggiore, and is utilised as a source of heat and light. Full analyses are given.

W. J. P.

Marly Limestones. By H. Le Chatelier (*Compt. rend.*, **118**, 262—264).—Marls and marly limestones are generally regarded as intimate mixtures of calcium carbonate with clay. The author has previously shown that true clay consists of a mixture of quartz with an aluminium silicate, $Al_2O_3,2SiO_2,2H_2O$, which is distinctly crystalline, loses water at about 600° if rapidly heated, and liberates heat suddenly at 950°. He finds, however, that the residues left after treating marly limestones with acetic acid never show the characteristic properties of true clays. They are richer in silica, although they contain no admixture of quartz; they lose their water at a lower temperature, show no sudden liberation of heat at a high temperature, and are sometimes amorphous, sometimes crystalline, but never show the crystalline form of true clay. The composition of the residue varies greatly with different marls; SiO_2, 51·6 to 66·1 per cent.; Al_2O_3, 16·1 to 21·2; Fe_2O_3, 3·6 to 7·2; H_2O, 9·0 to 19·5. The hydraulic limestone from the Congo leaves a residue which is distinctly crystalline, and has the composition $2MgO,4SiO_2,H_2O$.

C. H. B.

Occurrence of Diamonds in Meteorites. By O. W. Huntington (*Proc. Amer. Acad.*, **29**, 204—211).—In order to demonstrate that true diamonds occur in meteorites, the author dissolved many pounds of the Cañon Diablo iron in order to obtain enough diamond dust to use for cutting rough diamonds. About 200 lbs. of the iron was examined, and the most promising pieces were dissolved. About half a carat of diamond powder was finally obtained, being separated by its sp. gr. from a very large quantity of amorphous carbon.

The particles varied from colourless, through yellow and blue, to black. The diamond-cutting experiment was perfectly successful. The author's work establishes the fact that the Cañon Diablo iron contains true diamonds, and not any new allotropic form of carbon.

B. H. B.

Analyses of German Mineral Springs. By W. Thörner (*Chem. Zeit.*, **17**, 1411—1412).—The author gives the results of analyses of the water from (1) the Stahl spring, and (2) the Angelika spring at Tönnisstein, (3) the Wilhelms spring, and (4) the new spring at Melle, and (5) the sulphur spring at Levern. The results were as follows, in grams per litre.

	1.	2.	3.	4.	5.
$CaCO_3$..............	0·5285	0·4801	0·7373	1·1840	0·5632
$MgCO_3$.............	0·8660	0·7819	0·3437	0·1470	0·0550
$FeCO_3$..............	0·0162	0·0201	0·0149	0·1080	0·0001
Na_2CO_3............	1·0214	0·8820	—	—	0·0968
$NaCl$...............	0·2819	0·1880	21·7117	17·6790	0·1286
KCl................	0·0824	0·0741	0·0383	0·1290	—
$LiCl$................	0·0146	0·0127	—	—	—
NH_4Cl..............	0·0031	0·0041	—	—	—
Na_2SO_4.............	0·0927	0·0617	3·9121	3·1840	0·1330
$RbCl$...............	trace	trace	—	—	—
$MgCl_2$..............	—	—	0·6788	0·0950	—
Al_2O_3	0·0132	0·0056	0·0679	0·0045	0·0020
SiO_2................	0·0312	0·0293	1·1150	0·0800	0·0230
Organic matter	0·0067	0·0075	0·0186	0·0112	0·0280
CO_2	2·3844	1·9369	—	—	0·0610
$CaSO_4$..............	—	—	1·2894	1·7780	0·1180
$MgSO_4$	—	—	—	—	0·3480
K_2SO_4..............	—	—	—	—	0·0185
Na_2S	—	—	—	—	0·0390
H_2S................	—	—	—	—	0·0187

B. H. B.

Physiological Chemistry.

Changes of Substance in the Horse. By F. LEHMANN, O. HAGEMANN, and N. ZUNTZ (*Landw. Jahrb.*, **23**, 125—165; compare Abstr., 1889, 911; 1890, 1170).—The objection has been made to the authors' previous experiments that they were of too short duration for the accurate estimation of the changes of a whole day. The first experiments now described were made in a Pettenkofer apparatus, which consists of a large case, in which the horse is placed, provided with windows and with pipes, &c., so that the air may be withdrawn and renewed as required. These experiments lasted over 24 hours. The daily weight of the horse, the amount and composition of food and excrement were determined, as well as the amount of carbonic anhydride of the respiratory gases before and after ignition. Other experiments were made, in which the earlier method (obtaining the· gases directly from the trachea) and the Pettenkofer method were combined; these experiments lasted each about 10 hours. It was thus hoped to obtain trustworthy data as to the composition of the gases given off through the skin and intestines, inasmuch as the Pettenkofer method gives the total gases, and the trachea method the gases from the lungs alone. Earlier experiments on the skin respiration, as well as those made by Gerlach, seemed to indicate that the amount of carbonic anhydride so lost was very small, hardly more than 1 per cent. of that given off by the lungs.

The authors expressed the opinion in their former paper that the greater part (about three-quarters) of the intestinal gases were secreted through the lungs; this view, which was founded on Tacke's results ("Bedeutung der brennbaren Gase im thierischen Organismus," *Inaug. Diss., Berlin*, 1884), is now shown to be erroneous, as far as horses are concerned. Tacke's results, the correctness of which is not doubted, were made with rabbits, and cannot be applied to horses.

As regards the composition of the intestinal gases of horses, several samples of gas were directly collected for analysis. The collection of samples had to be done with great care, to avoid the admixture of air, as it was found that the pressure in the rectum is less than that of the atmosphere. The average percentage composition of four samples of intestinal gas was as follows.

CO_2.	CH_4.	H_2.	N_2.
22·49	59·92	2·59	15·00

Four more samples were taken from an old horse which had been fed for a week with oats (8 kilos.), hay (2 kilos.), and chaff (0·5 kilo. per day); the average composition was—

CO_2.	CH_4.	H_2.	N_2.
21·91	53·17	2·35	22·56

The horse was then killed, and samples of gas immediately taken from the cæcum and the colon. The composition of the gases was—

	CO_2.	CH_4.	H_2.	N_2.
From cæcum	78·70	5·29	0·89	15·12
From colon	72·74	17·28	0·84	9·14

In order to obtain evidence as to the nature of the gases evolved during fermentation after the horse was killed, weighed amounts of (1) the cæcum, (2) the colon, and (3) a mixture of fresh fæces with water were fermented, and the gases collected. The percentage composition was as follows.

	CO_2.	CH_4.	H_2.	N_2.
1......	95·96	0·75	2·91	0·38
2......	93·3	3·1	2·4	1·3
3......	58·47	0·89	36·96	3·68

The results obtained with gases collected immediately after the horse was killed, but especially these last results, differ considerably from those obtained by Tappeiner (Abstr., 1882, 240), which made it seem probable that the fermentation remained unchanged for some time after death. The present results show a distinct change in the character of the fermentation after death; the marsh gas almost disappearing (compare Ellenberger, *Physiol.*, 1, 808; Lungwitz, *Arch. wissens. u. prakt. Thierheilkunde*, 18, 87; and Schierbeck, *Arch. Hygiene*, 16, 203).

The following conclusions are drawn from the results of the experiments. The gases exuded by horses contain, besides carbonic an-

hydride, some methane, the amount of which is, however, consider-ably less than that produced by ruminants. The average daily amount of methane was 21·0 grams. Hydrogen was found (in these experiments) in only small quantities, not more than 1 gram per day. Most of the methane is secreted from the rectum, accompanied with about 37·5 per cent. of its volume of carbonic anhydride. Apart from the carbonic anhydride from the lungs, the horse lost daily 73·9 litres, of which 60·6 litres passed through the skin, 13·3 litres through the rectum. The skin respiration amounts to about 2·5 per cent. of the lung respiration. In the measurement of the lung respiration alone, there is an error of about −3 per cent. When this is taken into account, the results obtained in the experiments of short duration agree with the 24-hour experiments obtained with Pettenkofer's apparatus. As regards the practical management of horses, there is much evidence of the effect of disturbances in the change of substance. Thus, the irritation caused by the presence of a few flies in the apparatus caused an increase in the production of carbonic anhydride amounting to over 10 per cent. of the total formed by a resting horse.   N. H. M.

Effect on the Offspring of Calcium Phosphate, consumed during the Period of Gestation. By L. GRAFFENBERGER (*Jour. f. Landw.*, **41**, 57—64).—The results of Weiske's experiments (*ibid.*, 1888, 289) on the effect of calcium phosphate on the weight and composition of young rabbits showed an increase in amount of bone, free from fat, but there was no alteration in composition, and, in other respects, phosphate was without effect. According to Lehmann (*Ann. Chem. Pharm.*, **108**, 357) and v. Gohren (*Landw. Versuchs-Stat.*, **3**, 161), calcium phosphate is digested and assimilated by animals; Hoppe-Seyler (*Med. Chem. Untersuch.*, Heft 11) showed that, when mixed with human food, the salt is eliminated in the urine.

In the experiments now described, a litter of four rabbits, a week old, were killed with chloroform and analysed; the mother rabbit was then fed as before, but with addition of calcium phosphate (some grams per day), until a week after the birth of the next litter. The five young rabbits were then killed and analysed. Total weight, with and without skins, dry matter, fat, ash, lime, and phosphoric acid were determined. The results show that the calcium phosphate was without beneficial effect. The percentages of ash, lime, and phosphoric acid were somewhat diminished.   N. H. M.

Substitution of Strontium for Calcium in the Animal Organism. By H. WEISKE (*Landw. Jahrb.*, **23**, 119—123).—A reply to the portion of Haselhoff's paper (this vol., ii, 207) dealing with the animal organism. The author maintains that, whilst strontium is not a poison, animals fed with it, instead of with calcium, will not live, and that whilst strontium may be conveyed to the flesh and bones, &c., it is not a substitute, physiologically, for calcium (compare Cremer, *Sitzungsber. d. Ges. Morph. Physiol., München*, **7**, 124).
        N. H. M.

Excretion of Sulphur. By W. J. Smith (*Pflüger's Archiv*, **55**, 542—549).—In some sulphur-containing organic substances, the union of sulphur with carbon is so strong that the chemical decompositions accomplished in the body are unable to sever them. Such substances, of which acetone-ethylmercaptol and thiophen may be taken as instances, cause no increase in the sulphuric acid of the urine. The present experiments on a dog show that ethylic sulphide may be added to this list. The form in which the sulphur leaves the body was not, however, determined. These three substances have this in common, that the sulphur is combined thus, :C·S·C:. Nevertheless there are substances, such as carbamino-thioglycollic acid, containing the same combination of their sulphur which do give rise to an increase of urinary sulphates. W. D. H.

Human Pancreatic Ferments in Disease. By V. D. Harris and C. A. Crace-Calvert (*St. Barth. Hosp. Rep.*, **29**, 125—142).— 23 pancreases were examined, removed at varying periods after death from various diseases, and compared with the normal pancreas from a case of accident. The methods were those previously adopted by one of the authors (Abstr., 1893, ii, 22).

The number of cases is too small for general conclusions to be drawn. But the strength of the ferments was diminished in all cases, and markedly so in some. In a few cases, in children, it was impossible to show the presence of any ferments. The fat-splitting ferment was absent in about half the cases, the milk-curdling ferment in about half; the diastatic ferment was markedly diminished in brain cases, and to a less extent in all cases. The proteolytic ferment was the one least affected. It was, however, absent or feeble in cases of pneumonia, malignant disease, diabetes, and renal disease.

W. D. H.

Albuminous Periostitis. By L. Hugounenq (*Compt. rend.*, **118**, 149—150).—This rare disease is characterised by the accumulation under the periosteum of a liquid something like synovia. The liquid has a sp. gr. of 1·020 to 1·035, coagulates on heating to 80°, and contains a nucleo-albumin and an albumin resembling serum albumin. It frequently has fat droplets in suspension.

Quantitative analysis gave the following results.

Total solids	8·39	per cent.
Nucleo-albumin	0·87	,,
Albumin	5·61	,,
Succinic acid, urea, fat, and other extractives....................	0·98	,,
Ash	0·93	,,
Containing—		
Sodium chloride	0·43	per cent.
,, sulphate............	0·04	,,
,, phosphate	0·06	,,
,, carbonate	0·22	,,
Potassium chloride..........	0·08	,,
Calcium phosphate	0·05	,,

W. D. H.

Action of Selenium and Tellurium on the Animal Organism.
By F. CZAPEK and J. WEIL (*Chem. Centr.*, 1893, ii, 1098; from *Arch.
exp. Path. Pharm.*, **32**, 438—455).—No direct toxic action of selenium
compounds could be demonstrated on cells; but they act poisonously
on the animal body as a whole, and selenites more so than selenates.
The metal is not poisonous. It is probable that selenates are re-
duced to selenites in the body. Here there is an analogy to arsenic and
its compounds. The chief difference between selenium and tellurium
is in the way it leaves the body. Tellurium is more rapidly reduced to
the metallic state, which is harmless. Both elements, like arsenic,
act by weakening the heart, lowering blood pressure, and paralysing
the central nervous system. Antimony acts in a similar way.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Sulphhydric Fermentation in the Black Sea. By N. ZELINSKY (*J. Russ. Chem. Soc.*, **25**, 298—303).—The author has investigated samples of the ooze from the bottom of the Black Sea at depths of 16, 40, 389, 870, and 1207 fathoms, and from those dredged at the greater depths has succeeded in isolating various micro-organisms which possess the power of evolving hydrogen sulphide from the nutritive media in which they are cultivated. Amongst these there is one characterised by its great power of evolving hydrogen sulphide as well as by giving rise to a coffee-coloured pigment changing to black, when the microbe is cultivated in agar-agar. This microbe, which is a mobile, somewhat elongated bacterium, can live either in the presence or absence of atmospheric oxygen, and has been called by the author *Bacterium hydrosulfureum ponticum.*

The bacterium can evolve hydrogen sulphide not only from liquids containing proteïd matter, but also from media in which the sulphur is present as a component of an inorganic salt. Thus hydrogen sulphide is soon detected in liquids in which the sulphur has been added in the form of sulphates, sulphites, thiosulphates, or even ammonium thiodiglycollate. In the estuary at Odessa, a microbe (*Vibrio hydrosulfureus*), described by Brusilovsky, is active in the same way, reducing salts containing sulphur and oxygen to hydrogen sulphide. The other important product of fermentation is ammonia.

J. W.

Assimilation of Atmospheric Nitrogen by Microbes. By S. WINOGRADSKY (*Compt. rend.*, **118**, 353—355).—The following table gives the results of three series of experiments with cultures of the three bacilli previously described (Abstr., 1893, ii, 482—483). The nitrogen added to the cultures at the outset was in the form of ammonium sulphate.

1 {	Glucose in grams		2·0	4·0	2·0	2·0	10·0	20·0
	Nitrogen in milligrams { initial....	0·0	0·0	0·0	0·0	2·1	2·1
	{ increase..	5·9	9·7	3·9	4·9	15·7	24·4
2 {	Glucose in grams		1·0	2·0	3·0	4·0		
	Nitrogen in milligrams { initial....	10·6	10·6	10·6	10·6		
	{ increase..	0·0	0·8	3·7	4·1		
3 {	Glucose in grams		3·0	3·0	3·0	3·0	3·0	3·0
	Nitrogen in milligrams { initial....	2·1	4·2	6·4	8·5	17·0	21·2
	{ increase..	7·0	5·0	5·5	3·6	0·3	−2·2

It would seem that in media containing at the outset not more than traces of nitrogen, the quantity of nitrogen fixed is proportional to the quantity of glucose decomposed, but this ratio only holds good under strictly similar conditions. When nitrogen is present in the culture medium, the gain in nitrogen becomes much less regular, and a somewhat high proportion of glucose is necessary before any nitrogen is fixed at all. Further, even in presence of a high proportion of glucose, there is no gain in nitrogen if the initial proportion of this element exceeds a certain amount. The gain in nitrogen depends on the relation between the initial quantity of combined nitrogen and the initial quantity of glucose, and this ratio must be below 6 : 1000.

The bacillus which was regarded as the chief agent in fixing nitrogen (loc. cit.) was isolated by means of anærobic cultures on sections of carrot. When the pure bacillus is sown in the glucose culture fluid exposed to air in thin layers, it refuses to grow, and all the cultures remain sterile for an indefinite period; but if the two other bacilli (loc. cit.) or some mucedinæ are introduced, fermentation and the development of the specific bacillus begin at once. The anærobic character of the bacillus is further shown by its power of fermenting glucose in absence of air provided a small quantity of ammoniacal nitrogen has been added.

In order to obtain the maximum absorption of nitrogen, the pure bacillus should be introduced into a thin layer of glucose solution containing no combined nitrogen, but in contact with an atmosphere of pure nitrogen. In two experiments under these conditions, with 20 grams of dextrose, the gain of nitrogen was 28·0 and 24·7 milligrams respectively.

The bacillus does not germinate in broth or in gelatin. The chief products of the fermentation of the glucose are butyric, acetic, and carbonic acids and hydrogen, the gas that is given off sometimes containing as much as 70 per cent. of the latter.

It would seem that the absorption of free nitrogen is due to contact between this gas and nascent hydrogen within the living protoplasm, with the result that ammonia is formed.   C. H. B.

Nitrogen Question. By G. LIEBSCHER (*Journ. Landw.*, **41**, 139—198).—The chief object of the author's experiments was to ascertain how far Hellriegel's discovery that the *Leguminosæ* can utilise elementary nitrogen affects the cultivation of soils, Hellriegel's own results with senadella having indicated that the power of nitrogen fixation was much diminished in the presence of combined nitrogen. Inasmuch as in this case fixation was shown to depend partly on tho

manuring, it seemed not impossible that conditions might exist under which non-leguminous plants—mustard, for instance, which is extensively employed in green manuring—might also be found to have the power of assimilating free nitrogen.

In 1888, a series of pot experiments were made in which peas, oats, and buckwheat were grown in arable soil; peas and oats in humus sand and in poor sandy soil as well. In the case of the arable soil, there were also fallow experiments. The amounts of soil in each pot were—arable, 11,270; humus sand, 13,046; poor sand, 14,135 grams; containing 14·50, 11·17, and 7·12 grams of nitrogen respectively (or 0·1287, 0·0856, and 0·0504 per cent.). Some pots had an application of nitrate, others horn-meal, and the rest no nitrogenous manure. As regards oats, the yield in the unmanured pots was greatest in the poor sandy soil (61·59 grams of dry substance), next in the humus sand (53·25 grams), whilst in the arable soil the yield was only 30·70 grams, owing to the greater stability of the nitrogenous matter. The yield was greatly increased by nitrate in the arable soil, only slightly in the humus sand, whilst in the poor sandy soil there was less growth under the influence of nitrate than in the unmanured pots. In every case (but especially in the arable soil), the produce was richer in nitrogen where nitrate or horn-meal had been applied; in the oats grown in arable soil, the percentage was raised from 0·76 to 1·10 and 1·36 by nitrate and horn-meal respectively. As regards peas, the greatest yield and the most nitrogenous produce was obtained in the arable soil; in the poor sandy soil, both the yield and the percentage of nitrogen of the produce were diminished by the application of the nitrogenous manure. The arable soil gained nitrogen in every experiment. In the fallow experiments, the gain was as follows:—Unmanured, 0·5669 gram; horn-meal pot, 0·4402 gram; nitrate pot, 0 2711 gram. It is assumed that there was a loss in each case (more than covered by the gain due to algæ), which is the greater the more soluble the nitrogenous matter present. Deducting the gains of total nitrogen of the fallow pots from the total gains of the vegetation pots, the following average results, due to vegetation alone are obtained.

	No nitrogenous manure.	Nitrate.	Organic nitrogen.
Peas	+0·7331	+0·8986	+0·9092
Buckwheat .	—	+0·6511	+0·4419
Oats	+0·2571	+0·6070	+0·1496

Peas, therefore, collected the greatest amount of nitrogen.

The experiments with the two sandy soils showed a loss of nitrogen in the soil in every case, and a loss of total nitrogen in nearly every case; the losses were less with oats than with peas. The results indicate that the final amounts of nitrogen are greatest where the growth was most luxuriant, with peas in presence of little available combined nitrogen, with oats in presence of the greatest amount of available combined nitrogen.

The next experiments (1891–92) were conducted in zinc cylinders, closed at the bottom to prevent loss by drainage, and holding about

17 kilos. of soil (1891) and 10·6 kilos. (1892); the soils contained
0·1404 and 0·1469 per cent. of nitrogen. In 1891, there were four
fallow pots, six with oats, six with peas, and six with mustard; half
of the pots had nitrate (0·9528 gram of nitrogen), the rest no nitro-
genous manure, but the soil of each pot contained over 23 grams of
nitrogen. The following average amounts of air-dried produce and
nitrogen were obtained.

	No nitrate.		Nitrate.		Increase.	
	Produce.	N.	Produce.	N.	Produce.	N.
Oats............	67·2	0·4614	98·6	1·2176	31·4	0·7562
Mustard........	26·2	0·3584	54·6	1·3197	28 4	0·9613
Peas	60·5	1·1873	83·9	1·7552	23·4	0·5679

The percentage of nitrogen of the dry matter of the oats was
raised from 0·6867 to 1·2344 under the influence of nitrate; in
mustard from 1·3711 to 2·2973, whilst in peas there was no difference.
The nitrogen applied was utilised to the extent of 59·6 per cent. by
the peas, 79·4 per cent. by the oats, and 100·9 per cent. by the
mustard. The soil lost nitrogen in every case, and it is assumed that
there was no considerable gain by algæ. As regards total nitrogen,
the pea experiments nearly all show a gain, the others nearly all a
loss. The following table shows the average gain or loss of nitrogen,
and the effect of vegetation shown by the difference between the
fallow and vegetation pots.

	Without nitrate.		With nitrate.	
	Gain or loss.	Effect of plants.	Gain or loss.	Effect of plants.
Fallow.........	−0·6878	—	−0·8517	—
Oats...........	−0·3145	+0·3733	−0·2286	+0·6231
Mustard	−0·0255	+0·6623	+0·0333	+0·8850
Peas...........	+0·6852	+1·3730	+0·3852	+1·2369

Nitrogen fixation is thus only proved in the case of peas, but the
very considerable loss in the fallow pots (probably due to wetness
and want of aëration) makes it probable that there was also fixation
in the case of mustard.
  In 1892, the experiments were—fallow, peas (both without nitrogen-
ous manure, with mustard meal, and with nitrate), peas and mustard
mixed (with and without nitrate), haricots (with and without
nitrate), oats, oats and clover mixed, and mustard (all with nitrate).
One of the fallow pots had also mustard oil. The object of sowing

mustard with clover, and of manuring with mustard meal, was to ascertain whether the presence of mustard had any injurious effect on the soil organisms and consequently on nitrogen fixation. By growing oats and clover together, it was thought possible that the abstraction of combined nitrogen by the oats might induce an increased assimilation by the leguminous plant. The fallow soils showed a gain of nitrogen with the exception of those which had mustard oil and mustard meal, which lost, probably owing to the injurious effect of mustard on the algæ. On the other hand, neither the mustard plants growing with the *Leguminosœ* nor the mustard meal had any effect on nodule production. In all the vegetation experiments there was a loss of soil nitrogen but a gain of total nitrogen. Owing to the presence of algæ in the fallow pots, no comparison can be made between pots with and without vegetation. As before, the peas collected nitrogen, and to a greater extent in absence than in presence of nitrate. Owing to the richness of the soil, the clover grown with oats did not fix nitrogen to any extent, as is shown by comparing the results with those obtained with oats alone. Oats with nitrate collected more nitrogen than peas with nitrate, whilst mustard collected on the average twice as much as the peas. Peas and mustard mixed fixed the greatest amount of nitrogen, especially in those pots to which nitrate was applied; in these pots the fixation was raised 70 per cent. over that of the unmanured pots. There is evidence that the excess of total nitrogen of the mustard and peas over that of the peas grown alone is due to the mustard and not to increased assimilation by the peas.

It is concluded, as established, that there is only a difference in degree between the nitrogen-fixing power of the leguminous and the non-leguminous plants ; and it is probable that Frank's theory that all green plants assimilate free nitrogen is correct. The essential difference is that peas grow well and assimilate nitrogen when grown in soil poor in nitrogen, whilst in the case of non-leguminous plants, fixation is more or less dependent on the application of nitrogenous manure. This accounts for the negative results obtained with non-leguminous plants by Hellriegel and others, who employed sand free, or nearly so, from nitrogen, sometimes without and sometimes with very sparing addition of nitrate. Plenty of combined nitrogen must be given to these plants before they can assimilate free nitrogen, whilst *Leguminosœ* only require to be infected with nodule bacteria. As regards green manuring, a leguminous plant alone, mustard alone, or a mixture of the two, may be employed according to the conditions.

The method of analysis, which was carried out with great care, and the rather elaborate method of determining the error of analysis are given in detail. Large numbers of determinations were made in each case. As regards the experiments themselves, the most important error was the introduction of combined nitrogen by exposure to rain ; it is thought, however, that this is not at all considerable, but it will be avoided in future experiments. No attempt was made to ascertain the part played by the soil algæ, as, at the time the experiments were made, the author was not aware of their importance. The gains found in the vegetation pots of 1892, as compared with the fallow pots, can, at

any rate, not be due to algæ. It is suggested as possible that the gain of nitrogen in the pots sown with mustard, &c., may have been due to the co-operation of micro-organisms, but further experiments will be required to decide this point.   N. H. M.

Assimilation of Free Nitrogen by White and Black Mustard.
By J. P. LOTSY (*Exper. Stat. Bul.*, No. **18**, 1894).—White and black mustard were grown in pots in pure sand with minerals, and in water culture, both with and without nitrate. In the presence of combined nitrogen, the plants all grew well, and developed completely; but where no nitrate was given, the growth was slight, and the water culture plants died. The black mustard, however, which was grown without nitrate, developed more than the white mustard grown under the same conditions, indicating nitrogen-fixation. This may possibly be due to the vegetation of algæ.

Experiments made with the same plants, with and without nitrate under conditions of sterilisation, showed that whilst the nitrate plants grew well, those to which no combined nitrogen was given failed. Neither of the two species is, therefore, able to live in absence of combined nitrogen.

Sketches of the plants at different periods of growth, and of the apparatus, are given. No analyses are recorded.   N. H. M.

Functions of Hops used in the Dry-Hopping of Beer. By
H. T. BROWN and G. H. MORRIS (*Trans. Inst. Brew.*, **6**, 94—106).— The secondary fermentation which is brought about by adding a small quantity of hops to finished beer may be due to the occurrence in the hops of a fermentable sugar, an adherent "wild yeast," or an enzyme capable of hydrolysing the amyloïns and dextrin of the beer. The phenomenon is found by the author to be mainly due to the last-named cause. The enzyme is present in greatest quantity in the hop strobiles, but also occurs in the leaves and seeds of the plant (compare also Trans., 1893, 604). It was not isolated, for when the dried tissues are treated with a comparatively small quantity of water, sufficient tannin is extracted to prevent the enzyme passing into solution; when, however, a large quantity of water is used, the tannin forms such a dilute solution that it exerts little or no effect on the enzyme, which diffuses at a much slower rate.   A. R. L.

Invertase in Bananas.   By F. MIERAN (*Chem. Zeit.*, **17**, 1283).—
Ripe bananas contain invertase. An aqueous extract of the fruit made at ordinary temperatures, and afterwards digested at 55°, is lævogyrate $[\alpha]_D = -7 \cdot 15°$; a similar extract made at 100° is dextrogyrate $[\alpha]_D = +17 \cdot 49°$. Cane sugar in solution is hydrolysed by treatment with the ripe fruit, in one instance the rotatory power $[\alpha]_D = +99 \cdot 6°$ and $-11 \cdot 22°$, before and after the experiment respectively.   J. B. T.

Chemical Properties of the Alcoholic Extract of Beer Yeast.
By J. DE REY-PAILHADE (*Compt. rend.*, **118**, 201—203).—100 grams

of young pressed yeast containing 20 per cent. of dry matter is suspended in 55 grams of water containing a small quantity of glucose, and 45 grams of alcohol of 90° is added in successive small portions. A flask is filled completely with this mixture, stoppered, and allowed to remain at 0° with occasional agitation for three days. The contents are then filtered. and the filtrate passed through a d'Arsonval sterilising cylinder, and collected in a sterilised flask, which is made vacuous in order to remove the dissolved carbonic anhydride from the liquid.

The liquid thus obtained contains about 2·2 per cent. of alcohol, is slightly acid, and is free from living organisms. When brought in contact with sulphur, there is immediate formation of hydrogen sulphide; when heated at 45° in a sterilised and vacuous flask, carbonic anhydride is formed; when allowed to remain in contact with air, oxygen is absorbed, and carbonic anhydride is formed.

The alcoholic extract contains a considerable quantity of philothion, and attention is called to the similarity between the properties of this extract and those of extracts obtained from animal tissues.

<div style="text-align: right">C. H. B.</div>

Crystalloïds of Proteïn. By G. STOCK (*Ann. Agron.*, **20**, 105—106; from *Ber. Sachs. Ges. Wiss. Math. Phys.*, **150**, 638).—Acidified pepsin solution and a solution of pancreatin containing sodium carbonate both dissolve crystalloïds of proteïn. The crystalloïds disappear generally immediately before the death of leaves. Their production and solution does not seem to be affected by light. On growing plants in nutritive solutions, it was found that by withholding assimilable nitrogen, the crystalloïds may be made to disappear, whilst the addition of nitrogen in a suitable form causes their reappearance. In presence of plenty of nitrogen, a diminution in the quantity of calcium causes a considerable accumulation of crystalloïds. In the case of plants grown without lime, crystalloïds appear in parts of the plants where they never occur under normal conditions. Crystalloïds form in juices of leaves floated for some time on solutions rich in nitrogen.

<div style="text-align: right">N. H. M.</div>

Physiological Function of Calcium and Magnesium Salts in the Vegetable Organism. By O. LOEW (*Ann. Agron.*, **20**, 108—111; from *Flora*, 1892; *Bot. Centr.*, **51**, 152).—Calcium is present in plants as a precipitant for oxalic acid, and also as a protoplasmic compound in the chlorophyll grains. This is why the greenest parts of the plant contain most of the calcium. and is also a reason why those plants which produce no oxalic acid still require lime.

Potassium oxalate is extremely poisonous towards green plants, and causes remarkable changes in the chloroplast, of, for instance, *Spirogyra majuscula*, and a whole series of other algæ. It has no effect on mushrooms. Potassium tartrate and sulphate have no appreciable effect. It is suggested that the oxalic present in plants liberates the lime from the protoplasmic compound causing the modified chlorophyll grains to swell—that was the effect observed

under the influence of potassium oxalate—and the albumen to pass from the active to the passive state. Oxalic acid itself is by far the most poisonous organic acid towards plants ; a 0·004 per cent. solution causes the nucleus to swell, and to become opaque. It seems likely that calcium compounds have an important part in the nucleus, that a compound of calcium with nuclein forms the framework of the nucleus. If this is the case, the nuclei of lower fungi must be differently constituted, as oxalic acid has no effect on them. If it is admitted that such calcium compounds exist, the important effect of calcium in the transport of starch becomes more intelligible.

With regard to magnesium, the first question which arises is why it cannot be replaced by calcium. The reason is probably that magnesia is a very feeble base, and can be much more readily separated from acids than is the case with lime. This explains the injurious effect of magnesium salts when given alone to plants. Calcium salts when present prevent any injurious effect from magnesium salts, whilst sodium and potassium salts remain without effect; the magnesium salts then show their nutritive property, which depends on the ease with which they give up their acids, especially phosphoric acid. The tertiary phosphate of magnesium accumulates where the nuclein and lecithin are produced, and hence magnesia, like phosphoric acid, follows the proteïds which accumulate in the seeds. This only holds good in the case of green plants. Just as in the case of lower vegetation, oxalates are not injurious, so also magnesium salts have no injurious effect on them in absence of lime.

<div align="right">N. H. M.</div>

Substitution of Strontium for Calcium as Plant Food. By E. HASELHOFF (*Landw. Jahrb.*, **22**, 851—861).—Hitherto experiments on the substitution of strontium for calcium have only been made with animal food. Papillon (*Compt. rend.*, **71**, 372) showed that such a substitution may take place in bones. This was disputed by Weiske (*Zeit. Biol.*, **8**, 239). J. König, however (*Landw. Jahrb.*, **3**, 421), in experiments with rabbits came to the same conclusions as Papillon.

As regards plants, no experiments had as yet been made, although the question is one of some importance to agriculture, especially in Westphalia, where some soils contain considerable amounts of strontianite. The author grew barley and beans in a poor sandy soil, to which calcium and strontium carbonates respectively were added ; he also grew beans and maize in nutritive solutions containing calcium and no strontium, and *vice versâ*. The results show that strontium has no injurious action on plants; that it is taken up by plants, and seems to take the place of lime ; and that it replaces lime only when the supply of lime and other substances are no longer adequate for the wants of the vegetable organism.

<div align="right">N. H. M.</div>

Ash Constituents of the Coffee Tree. By F. W. DAFERT (*Landw. Jahrb.*, **23**, 27—45).—The analyses were made in the Agricultural Institute of São Paulo, Brazil, the common coffee tree of the country being employed. The percentage results are given on p. 208.

It is noteworthy that the percentage of potash increases with the distance of the organ from the root, being highest in the leaves, and

<div align="right">17—2</div>

that the lime is highest in the root, and diminishes with the distance
from the root.

	Roots.	Stems.	Branches.	Leaves.	Husks.	Beans.
Pure ash in air dry substance	4·78	1·44	3·25	5·10	3·80	2·84
In pure ash—						
K_2O	28·24	44·03	49·20	56·48	54·46	62·99
Na_2O	3·28	1·92	0·58	1·43	2·03	—
CaO	18·99	18·99	33·03	21·65	10·20	5·18
MgO	8·58	9·35	7·62	6·57	4·35	11·45
Fe_2O_3	12·95	1·91	2·08	0·90	5·61	0·57
P_2O_5	4·21	4·49	4·52	6·07	4·44	14·16
SO_3	4·61	2·10	1·94	3·51	2·98	5·05
SiO_2	16·37	(0·45)	0·83	2·17	13·67	0·30
Cl	1·63	(0·24)	0·61	0·51	0·60	0·33

N. H. M.

Physiological Action of Tellurous Acid. By T. BOKORNY
(*Chem. Zeit.*, **17**, 1598—1599).—The aqueous solution of this sub-
stance has no action on various algæ and infusoria. Its solubility in
water is very small, and may be assisted by the addition of dipotas-
sium phosphate. Under these circumstances, the solution is harmless
to the organisms in question, and the histological appearances in cells,
nuclei, chlorophyll granules, &c., are described as perfectly normal.
Selenious acid is more poisonous, and sulphurous acid more poison-
ous still.   W. D. H.

Injurious Action of Nickel on Plants. By E. HASELHOFF
(*Landw. Jahrb.*, **22**, 862—867).—Three soils from meadows which
had been irrigated with contaminated waters, were found to contain
copper oxide (0·63, 0·89, and 2·05 per cent.), zinc oxide (0·95, 0·83,
and 0·60 per cent.), and nickel oxide (0·12, 0·20, and 0·15 per cent.,
reckoned in soil dried and free from humus). In order to ascertain
the effect of nickel on plants, horse beans and maize were grown in
nutritive solutions to which nickel sulphate was added in various
amounts, containing from 2·5 to 50 milligrams of nickel oxide per
litre. The smallest amount (2·5 milligrams per litre) was sufficient
not only to stop growth but to kill the plants.   N. H. M.

**Composition of Algæ and other Marine Plants of the Coast
of Algeria.** By J. A. MULLER (*Ann. Agron.*, **20**, 82—91).—In the
coast districts of Algeria, algæ are employed for manuring. They are
first exposed to rain to wash out the salt, and dried in the sun, or else
applied directly after they are sufficiently washed out. Sometimes after
being washed by rain they are burnt, and the more or less carbona-
ceous ash used as manure. The plants examined by the author were
collected at the Cape of Acrata, near Guyotville. Eleven species were
examined, and the results of the nitrogen estimations and ash analyses

are tabulated in the original. The nitrogen varied from 0·75 to 1·83 per cent. of the dry matter in different species.   N. H. M.

Digestibility and Nutritive Value of various Grains. By H. WEISKE (*Landw. Versuchs-Stat.*, **43**, 207—222).—It has already been shown that oats are digested by rabbits in varying amounts, being most thoroughly digested where small amounts were consumed (*Landw. Jahrb.*, **21**, 791, and Abstr., 1893, ii, 132). The experiments now described were made with sheep, which were first fed with 500 grams of air-dried oats daily. This experiment lasted for about a week, when they had to be discontinued as the sheep began to leave some of the food uneaten. During the experiment, the sheep took very little water; instead of about 2·5 parts of water to 1 of dry food, which is the usual amount, the consumption of water to dry food was only 1·2 and 0·8 : 1. The production of urine was very small, especially in the case of sheep No. 2 (average 40 c.c. daily); but the percentage of water in the fæces was high, especially towards the end of the experiment. Deducting the amounts of the various constituents of the fæces from those of the 500 grams of oats given daily, the following percentage amounts are found to be digested by the sheep 1 and 2.

	Dry matter.	Nitrogenous matter.	Ether extract.	Crude fibre.	Non-nitrogenous extract.
1	79·5	78·4	88·3	52·9	86·4
2	72·6	61·3	85·1	48·3	81·5

Sheep No. 1 digested the oats in the quantity given better than the large amount previously given (*loc. cit.*); sheep No. 2 digested more fat and crude fibre with the less amount of food, but not so much nitrogeneous matter. It is probable that the nature of the individual sheep has a good deal of influence on the results. Much depends on the more or less complete chewing of the food, which, in this case although sufficiently nourishing, is very much wanting in bulk.

Experiments were next made in which the amounts of barley and rye digested by rabbits were determined. The results, together with those previously obtained, show that, under similar conditions, rabbits digest oats better than either barley or rye, as regards the two most important constituents, proteïn and fat. The difference in the percentage amounts digested is shown in the following table.

	Dry matter.	Organic matter.	Proteïn.	Fat.	Crude fibre.	Nitrogen free extract.	Ash.
Oats....	73·7	74·5	80·2	93·8	21·6	79·5	46·4
Barley ..	84·0	85·4	67·7	86·3	25·1	91·2	51·2
Rye	84·4	85·4	63·0	76·3	18·5	91·2	34·4

The percentages obtained with barley are lower as regards proteïds and fats than those given by Wolff for horses and sheep, whilst the non-nitrogenous extract is higher.

The value of oats is, compared with barley and rye, probably due in part to the greater digestibility of its proteïds and fat.

N. H. M.

Influence of Nitrogenous Manures on Grass. By Woods and Phelps (*Bied. Centr.*, 1894, 90—91).—During 1890—92, nitrogenous manures were applied to unmanured land on which the crop growing consisted mainly of Timothy, smooth-stalked meadow and Fiorin grasses, whereby an increase of yield was obtained, whilst on a plot treated with minerals only, the clovers were increased. In addition to the increase of yield of hay produced by the nitrogen, the composition was also affected, as a higher percentage of proteïds was obtained. On the plot manured with minerals (bone superphosphate and potassium chloride), the proteïds were highest owing to the extra growth of the clovers. Excessive nitrogenous manuring is wasteful. Thus a plot which in the three years had received 84 kilos. of nitrogen yielded hay containing 139 kilos. of nitrogen, but another plot which had received 252 kilos. only returned 229·8 kilos. of nitrogen in the hay. E. W. P.

Efficiency of the most important Preservatives of Stable Manure. By H. Immendorff (*Journ. f. Landw.*, 41, 1—56).—The object of the experiments was to ascertain the effect of different calcium phosphates mixed with gypsum on the decomposing manure. For this purpose, damp meat-meal and blood-meal, mixed with ground grass or clover leaves, were treated with mixtures of the pure calcium salts mixed with gypsum, at a constant temperature of 30°, in a suitable apparatus, so that the changes could be observed, and gaseous products collected. The two substances, meat-meal and blood-meal, were selected rather than fæces and urine, owing to the greater ease with which accurate analyses of them can be obtained. After observing the effect of pure salts, experiments with commercial phosphatic manures were made. The apparatus was similar to that employed in earlier experiments (Abstr., 1892, 374), but somewhat simpler.

In the first series, 15 grams of meat-meal mixture (containing 0·6848 gram of nitrogen) was used for each experiment; in the second series, 15 or 10 grams of blood-meal mixture (containing $N = 0.666$ and 0·444 gram). In both series, an equal weight of gypsum was added, besides the phosphates. In the third series, blood-meal mixture (20 grams) was mixed with a phosphatic manure alone. Tables are given showing the total and final amounts of nitrogen, the final amount of nitric nitrogen, and the final amounts of nitrogen as ammonia remaining in the material experimented on, and as that collected in the receiver, representing the loss which would take place in the open air. As regards changes in the total nitrogen, there was in no case (in the 20 experiments) a loss which could not be accounted for by the experimental error, and only in two cases a gain.

The table on page 211 shows the percentage of the nitrogen as ammonia which volatilised (which is the most important of the results), and the nitrogen as ammonia, which was fixed. Series I includes Nos. 1—8; Series II, 9—12; and Series III the rest.

The experiments 13 to 20 were made in pairs, alike as regards minerals added, but different as regards amount of ventilation, Nos. 14, 16, 18, and 20 being very slightly ventilated.

As regards nitric nitrogen at the end of the experiment, none was

	Nitrogen as ammonia.	
	Volatilised.	Fixed.
1. $Ca_3(PO_4)_2$ (3)	7·75	67·96
2. „ (1·5)	9·43	59·46
3. $Ca_2H_2(PO_4)_2$:(P_2O_5 = 1·8)...............	14·46	58·69
4. „ („ 0·9)...............	13·36	60·69
5. $CaH_4(PO_4)_2$(P_2O_5 = 0·6)	2·40	62·11
6. „ („ 0·3)	6·98	56·08
7. H_3PO_4(0·551)	4·81	62·75
8. „ (0·276)	11·84	63·60
9. $Ca_2H_2(PO_4)_2$·(P_2O_5 = 1·8)...............	6·25	31·26
10. „ („ 0·75)	1·11	46·41
11. H_3PO_4(0·455)	0·79	48·22
12. No phosphate.........................	7·21	39·21
13. Containing P_2O_5. (a) 8·99, (b) 3·33, (c) 1·92*	7·13	35·98
14. „ „ „ „ „	1·29	34·20
15. „ „ (a) 9·62, (b) 2·96, (c) 6·2..	0·0	44·22
16. „ „ „ „ „ ··	0·0	40·54
17. „ „ (a) 8·11, (b) 1·72, (c) 6·2 .	0·0	28·68
18. „ „ „ „ „ ·	0·0	22·79
19. „ „ (a) 13·83, (b) 1·73, (c) 11·5	0·0	48·52
20. „ „ „ „ „	0·0	50·17

* (a) total, (b) soluble in citric acid, (c) soluble in water.

found in experiments 1—12, and 16, whilst in the other experiments the following amounts, in percentages of total nitrogen, were found. (13), 1·39; (14), 0·40; (15), 0·60; (17), 1·94; (18), 1·23; (19), 1·59; (20), 1·15. The greatest amounts of nitrate were therefore formed when the ventilation was greatest. Its production is clearly not necessarily attended with a loss of nitrogen.

The results of the experiments show that the fixing power of gypsum for the ammonia of decomposing organic matter is considerably increased by free phosphoric acid and calcium monophosphate, that is, by phosphates soluble in water. Tricalcium and dicalcium phosphates are without effect. Superphosphate gypsum loses its fixing power to some extent through the water soluble phosphate becoming insoluble (soluble in citric acid), but not appreciably. It also seems to hinder the processes which give rise to the elimination of free nitrogen. Stassfurt salts suppress ammonia production to some extent, but seem to increase loss of free nitrogen. Kainite enriches the manure in potash and magnesia, and preserves the organic matter; but it is said to injure the hoofs of animals, and injures the manure for certain crops. Kainite and superphosphate gypsum gave good results, preventing both loss of ammonia and of

free nitrogen; the presence of superphosphate gypsum seems to compensate for the otherwise bad effect of the kainite. The addition of chalk to decomposing organic matter nearly always causes great production and loss of ammonia.　　　　　　　　　　N. H. M.

Changes in, and Effects of, Irrigating Water. By E. FRICKE, E. HASELHOFF, and J. KÖNIG (*Landw. Jahrb.*, **22**, 801—849).—In former communications, the effects of various waters under various systems of meadow cultivation were discussed (*ibid.*, **6**, 287; **8**, 505; **11**, 151; and **14**, 177). In the present paper, the results of experiments with the same water on various soils are given.

A. *Irrigation with Ordinary Water.*—The experiments were conducted in large cases built of stone and cement. These were more than half filled with gravel, over which was the layer of sandy, loamy, calcareous, and peaty soil respectively. There were three cases for sandy soil irrigated (*a*) with the same amount of (Münster) water as the other cases; (*b*) twice the usual amount; and (*c*) the same amount of Münster water, but diluted with distilled water. This was to ascertain the effect of a pure water as compared with the Münster water alone, which is very rich in minerals. The temperature of the soils at different depths was observed, and there were arrangements for collecting drainage. The boxes were irrigated first in July, 1885 (the year after the grass was sown), and at five subsequent periods, of which the last was June, 1887. The irrigation was for about four days at a time. The surface drainage and that which passed through the soil were examined. Tables are given for each period, showing the amount and composition of the water applied, as well as the surface and other drainage from each soil. As regards the surface drainage, the amount of oxygen it contains is less than the original water, the decrease being greatest in the case of soils which contain the most organic matter. The carbonic anhydride and lime go together. The lime decreased considerably in the case of peaty soil, and slightly in the case of sandy soil, whilst in passing over calcareous and loamy soils the water became richer in lime. Magnesia, on the other hand, was taken up by the water from the peaty soil, and deposited to a slight extent in all the other soils. In every case, the water lost a good deal of nitric acid. The nutritive matters of irrigating water are not absorbed to any extent by the soil, but mainly by the plant directly, and the loss or gain in any constituent will depend on the wants of the plant and the presence of an excess or deficiency of the constituent in the soil. In warm weather, the surface drainage takes up more organic matter, but not always more carbonic anhydride, than in cold weather; in the case of peaty and sandy soils, which are poor in lime, the summer drainage contains less carbonic anhydride (and less lime) than the winter drainage. On the other hand, the surface drainage from the loamy and calcareous soils is richer in lime in warm than in cold weather. The quantity of nitrates is greater in summer drainage (except in the case of the loam) than in winter drainage; generally poor soils will respond most to irrigation, especially when vegetation is most active. Frequent but slight irrigation (to avoid surface drainage) during summer is recommended.

Night surface drainage contained more organic matter than the day drainage, probably due to a greater secretion of organic matter from the roots during the night. The peaty and sandy soil drainage contained less lime in the day time than in the night, whilst the reverse holds good in the case of the calcareous and loamy soils. The drainage through the soil generally behaves like the surface drainage. It contains less nitric acid than the surface drainage, showing that the deeper roots take up considerable amounts of food; and there is a general diminution of bases, that is to say, for 1 part of base the drainage contains more acid than the irrigating water and the surface drainage. The following numbers show the amount of acid to 100 base (1) in the surface drainage, and (2) in the drainage.

	Peaty soil.	Calcareous soil.	Loamy soil.	Sandy soil.
1	167	166	165	169
2	179	168	165	210

The relation in the water as applied was 100 : 164.

There is no definite relation between evaporation and kind of soil, evaporation depending chiefly on the amount of vegetation, sunshine, and the wind (compare Masure, *Landw. Jahrb.*, 1882, 191; Eser, *ibid.*, 1885, 208; Battelli, *Il Nuovo Cimento*, 1890, [3], **28**, 247). Comparative experiments were made on the evaporation from a surface of water, from a soil containing 65 per cent. of the total amount of water it would hold, and from soil sown with grass. The relations in amount of evaporation were 100 : 65 : 202.

The amount and composition of the grass cut in 1886 and 1887 are given, as well as that in 1888 after irrigation with sewage water. As regards the crops of 1886 and 1887, the results show that the soils lost both nitrogen and potash, the amounts of these two constituents of the irrigating water being insufficient. Lime was deposited both in the peaty and sandy soils, but the calcareous and loamy soils both lost lime. In the case of magnesia, just the opposite takes place. Sulphuric acid was deposited in every case in excess of the amount found in the produce; it is probable that it was taken up by the roots as a reserve for future growth. The behaviour of lime and magnesia indicates a similar storing by the roots. The produce obtained under the influence of sewage water was richer in nitrogen, potash, and phosphoric acid than that of the two previous years.

The soils which benefit most in ordinary irrigation are the poor sandy soils; peaty soils are also improved, especially by water rich in lime (compare Fleischer, *Hannov. Landw. u. forstw. Zeit.*, 1884, 841; Egger, *Chem. Centralbl.*, 1887, 525, and *Trost. Ann. Soc. Geol. Belg.*, **11**, 123).

B. *Irrigation with Sewage Water.*—These experiments were similar to those described above. The four different soils were employed. The sewage was mixed with tap water in the proportion 80 : 585. There were four applications from November, 1887, to March, 1889. The following table shows the average composition of the water as applied, and of the drainage, in milligrams per litre.

	Sewage water applied.	Drainage.			
		Peaty soil.	Cal-careous soil.	Loamy soil.	Sandy soil.
O_2 required for oxidation..	125·2	14·2	13·8	12·7	10·5
CO_2.....................	490·7	106·5	225·7	236·5	107·1
CaO	122·4	121·0	177·7	196·2	116·4
MgO	15·5	18·5	13·8	14·8	13·9
K_2O.....................	66·3	29·2	33·5	23·7	20·8
Na_2O	99·2	56·5	55·7	59·0	54·1
Cl	134·4	111·9	91·4	97·6	92·8
HNO_3...................	18·8	81·0	86·0	85·2	114·8
SO_3...................	63·2	55·1	58·6	52·0	49·2
P_2O_5...................	14·0	0 − 1·3	0 − 1·3	0 − 1·0	0 − 0·5
Ammoniacal nitrogen	119·8 }	{ trace	{ trace	{ trace	{ trace
Organic nitrogen	31·0 }	{ − 12·7	{ − 12·4	{ − 7·3	{ − 3·1

Other experiments were made in which the sewage water was applied very frequently instead of at long intervals. The results of both sets of experiments show that the sandy soil is the most suitable, owing to its greater permeability for air. If insufficient air is present, a reduction of nitric to nitrous acid takes place, and loss both of nitrogen and sulphur. For complete oxidation of the sewage, vegetation is necessary, and it is important to avoid an excess of sewage. To utilise the nitrogen of the sewage, about twice as much phosphoric acid and three times as much potash are required as the sewage contains. The vegetation of 1 hectare of soil will take up, at the most, 300 kilos. of nitrogen, corresponding with the sewage from about 60 to 80 of the population.

C. *Irrigation with Impure Water containing Salts.*—The waters with which all four soils were successively irrigated in these experiments contained :—(1) nothing added ; (2) NaCl, 0·1 per cent. ; (3) $CaCl_2$, 0·1 per cent. ; (4) $MgCl_2$, 0·1 per cent. ; (5) $FeSO_4$, 0·03 per cent.; (6) $ZnSO_4$, 0·02 per cent. ; and (7) $CuSO_4$, 0·02 per cent. There was further dilution from rain. The application of common salt gave rise to an increased loss of lime, magnesia, and potash. Calcium chloride caused a deposition of lime in soil or plants and a loss of other bases (MgO, Na_2O, and K_2O). Magnesia, iron, zinc, and copper were all deposited, more or less, whilst the drainage removed other bases.

N. H. M.

Analytical Chemistry.

Estimation of Sulphur in Regenerated Gas-Purifying Material. By F. MEYER (*Chem. Zeit.*, **17.** 1319).—A few grams of the material is wrapped up in a filter and placed inside the bulb of a calcium chloride tube, which is then connected with a 150 c.c. round-

bottomed flask containing about 30 c.c. of carbon bisulphide. The top part of the tube is then connected with a reflux condenser. A Soxhlet's apparatus may, of course, be used instead of the calcium chloride tube. After heating the flask in a water bath of 80° for about an hour, the sulphur will be completely extracted. The flask is disconnected, the carbon bisulphide distilled off, and the residual sulphur finally oxidised by nitric acid and potassium chlorate.

L. DE K.

Estimation of Free Acids in Salts of the Heavy Metals. By F. HOFFMANN (*Chem. Zeit.*, **17**, 1318—1319).—The author adds to the solution of the metallic salt, copper sulphate for instance, a very slight excess of potassium ferrocyanide, and then makes up to a definite bulk. After the precipitate has completely settled, an aliquot part of the liquid is syphoned off, and the free acid titrated with N/10 soda, using phenolphthalein as indicator. When the precipitated ferrocyanide is colourless, as in the case of lead, silver, or zinc, a moderate excess of ferrocyanide is not injurious, and the liquid need not be filtered before titrating. To be successful, the metals should be in the highest state of oxidation, the process failing, for instance, with ferrous sulphate.

L. DE K.

Precipitation of Barium Sulphate in Presence of Silica and the Decomposition of Barium Sulphate by Hydrofluoric acid. By J. F. SLEEPER (*Chem. News*, **69**, 63—64).—It is shown that barium sulphate precipitated in the presence of sodium silicate is in no way contaminated; moreover, that barium chloride does not give a precipitate in a solution of sodium silicate. The suggestion of removing silica from barium sulphate by means of hydrofluoric acid is found to be untenable, inasmuch as mere evaporation with this acid is sufficient to decompose the sulphate, occasioning loss, which increases with the augmentation of the volume of the acid used; this decomposition is prevented by large, but not by small, quantities of free sulphuric acid.

D. A. L.

Colorimetric Estimation of Iron. By A. ZEGA (*Chem. Zeit.*, **17**, 1564—1565).—For the estimation of iron in waters, the author recommends the following method. To 100 c.c. of the water (in which the iron has already been oxidised to the ferric condition) 1 c.c. of nitric acid (sp. gr. 1·35—1·40) and 5 c.c. of a 5 per cent. solution of potassium thiocyanate are added. The coloration develops rapidly, and does not darken on remaining. 100 c.c. of distilled water is then similarly treated, and a standardized solution of a ferric salt containing 0·01 milligram of iron per c.c. run in until the coloration produced is equal to that in the water under examination. The quantity of ferric solution added represents, of course, the quantity of iron in the water. In this way 0·01 milligram of iron per 100 c.c. of water is easily estimated.

L. T. T.

Estimation of Nickel. By J. F. SLEEPER (*Chem. News*, **69**, 15—17).—To avoid the uncertainty incident to prevailing methods of

estimating nickel, the author has adopted the following modes of procedure.

Shot or plate nickel is broken up as far as possible, avoiding the introduction of adventitious iron, and 20—25 grams is dissolved by heating gently with 250 c.c. of dilute (1 : 1) nitric acid, the fumes being subsequently boiled off. The solution is made up to 2 litres and 50 c.c. evaporated to dryness with hydrochloric acid.

Mattes or ores are dissolved in aqua regia, and evaporated to dryness with hydrochloric acid ; taking 1 to 5 grams, according to richness.

Speiss, 1 gram, is treated with aqua regia and frequent additions of a saturated solution of potassium bromide in water charged with excess of bromine, and is then evaporated to dryness with hydrochloric acid.

In these three cases the solutions, after evaporating to dryness with hydrochloric acid, are redissolved in this solvent, diluted, and the proportion of hydrochloric acid made up to one-eighth or one-tenth of the total volume.

Nickel oxide is reduced to an impalpable powder, dried at 130°, and 1 gram is heated gradually to, and then at, redness with sodium hydrogen sulphate, in a partially covered crucible, until action ceases, then, when sufficiently cool, about 2 c.c. of concentrated sulphuric acid is added, and the heating is resumed until the whole mass becomes liquid. When cool, it is dissolved in hot water (any residue being ignited and re-treated), and 7 to 10 c.c. of hydrochloric acid is added to the solution, the volume of which should be from 75 to 100 c.c.

A solution prepared by any of these methods is treated, while hot, with hydrogen sulphide, filtered, and the precipitate washed with hydrogen sulphide solution ; the filtrate, after removing the hydrogen sulphide completely by boiling, is boiled for a further five or ten minutes with nitric acid, and, while boiling, is gradually and cautiously precipitated with excess of caustic soda, as free as possible from carbonate and alumina ; the boiling is continued for 15 minutes longer, and after 15 minutes' standing on a water bath, filtration is proceeded with ; the precipitate being thoroughly washed with boiling water, by digesting with it, as well as on the filter, before being dissolved in hot dilute sulphuric acid (1 : 15 or 20 of water) ; the total amount of sulphuric acid used in this and subsequent re-treatments should not, however, exceed 10 c.c. The solution is diluted to from 150 to 300 c.c., according to the quantity of iron present, and when cold is treated rapidly with excess of concentrated ammonia, allowed to settle, the supernatant liquid filtered off, the precipitate washed with water, redissolved in the dilute sulphuric acid and reprecipitated with ammonia, these operations being repeated two or three times if much iron is present. The combined filtrates are evaporated to 50 to 75 c.c., at a low temperature, to avoid drying up or the separation of any nickel salt, and the concentrated solution treated, as soon as convenient, with ammonia, using 5 c.c. in excess of that required to produce a blue colour, any precipitate is filtered off, redissolved, and reprecipitated, &c.; 25 c.c. of strong ammonia is added to the filtrate, which is diluted to 200 c.c. and electrolysed,

using cylindrical platinium electrodes supported at $\frac{1}{5}$ to $\frac{1}{16}$ of an inch above the bottom of the glass. There must be plenty of ammonia present; not too much sulphuric acid, and no nitrate, alumina, or iron. After use, the electrodes are cleaned by immersion in hot dilute nitric acid. D. A. L.

Estimation of Chromium in Chrome-Steel and Chrome-Iron Ore. By J. SPÜLLER and S. KALMAN (*Chem. Zeit.*, 1360—1361; 1412).—Two grams of steel borings is dissolved in 16 c.c. dilute sulphuric acid (1—5) contained in a hemispherical dish of 300 c.c. capacity, and covered with a watch-glass. When effervescence has ceased, the glass is removed, rinsed with a little hot water, and the whole evaporated to dryness with constant stirring. When dry, the mass is calcined and then mixed in a silver basin with 4 grams of powdered sodium dioxide and 8 grams of sodium hydroxide. On heating the mass, frothing takes place at first, but this soon ceases when the contents are stirred with a silver spatula. The fusion is now continued for 15 minutes, when 4 grams of sodium dioxide is added; after 20 minutes' further heating another 2 grams of this substance is added; after the lapse of $1\frac{1}{4}$ hour, the whole of the chromium is converted into sodium chromate. When cooled a little, the basin is freed from soot, placed inside a porcelain dish, and lixiviated with water. The further operations are the same as described in the authors' process for the estimation of chromium in ferrochrome (compare this vol., ii, 70).

Chrome-iron ore may also be analysed by direct fusion with the sodium dioxide mixture. L. DE K.

Electrolytic Estimation of Lead. By A. KREICHGAUER (*Ber.*, **27**, 315—318; compare Medicus, Abstr., 1892, 1522).—The nitric acid, used in making the solution of lead nitrate to be electrolysed, should consist of 1 part of acid of sp. gr. 1·4 to 7 parts of water; the deposited lead dioxide should be washed twice with alcohol and dried for five minutes at 120°. It is slightly hygroscopic owing to the presence of a trace of nitric acid, which is difficult to remove; the amount of water taken up is, strange to say, independent of the weight of the dioxide. C. F. B.

Analysis of Phosphor-tin. By C. A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, **12**, 262—267).—About 1 gram of the substance is introduced in small pieces (2—4 per gram) into a flask of 60—80 c.c. capacity; 40—50 c.c. of water is added, and the mouth of the flask covered by a funnel; 5 c.c. of purified liquid bromine is now added in 3 to 4 portions; about 1 c.c. of bromine is added at first, the flask being placed in a bath of cold water. Although the reaction proceeds with the production of flame, it must not be too rapid, and rise of temperature must be avoided, otherwise a gelatinous deposit of stannic oxide is produced. The whole operation of adding the bromine takes 5—10 minutes. If small particles of the substance remain unattacked, more bromine is added, the mixture gently heated on the water bath, and subsequently allowed to remain for some time. The solution is transferred to a porcelain capsule, the flask rinsed with

concentrated hydrochloric acid, the solution diluted with an equal volume of water, and the bromine is expelled by evaporation on the water bath. The concentrated hydrochloric acid serves to dissolve any stannic oxide. The solution must not be concentrated too much, or tin will be volatilised. The tin is estimated by precipitation as sulphide or by Classen's electrolytic method, whilst the phosphorus is estimated in the filtrate from the tin as magnesium pyrophosphate.   A. R. L.

Paraffin Estimations. By R. Höland (*Chem. Zeit.*, **17**, 1473, 1483—1484).—The author has proved by a series of experiments that paraffin may be quantitatively separated from yellow oil (a product of the dry distillation of brown coal) by treating the sample with 10 times its bulk of commercial absolute alcohol and subsequently cooling in ice-cold water for about two hours. If, however, the amount of paraffin is less than 20 per cent., it is advisable to first remove the bulk of the oil by a fractional distillation.

The precipitated paraffin is collected on a weighed filter contained in a double funnel cooled with ice, and washed with cold alcohol. It is then freed from the bulk of alcohol by squeezing between blotting paper, and finally dried at 100° on a weighed watch-glass.
                                                                  L. DE K.

Analysis of Mixtures of Sperm Oil and Mineral Oil. By C. A. LOBRY DE BRUYN (*Chem. Zeit.*, **17**, 1453).—The author uses the process recommended by Allen and Thomson, but has made a slight modification. 5 grams of the sample is boiled for some hours with a solution of 2 grams of sodium hydroxide in 25 c.c. of absolute alcohol. The liquid is diluted with water and shaken twice with light petroleum, which is then washed with water and finally distilled off in a weighed flask. The contents are, after weighing, boiled with twice the volume of acetic anhydride. Complete solution takes place, but, on cooling, the mineral oil separates almost entirely, and can be readily removed from the acid. The author finds, however, that it retains a small proportion of acetic acid, which causes it to solidify in contact with metallic sodium; it is therefore necessary to agitate it with a weak alkali and again dissolve it in light petroleum. After distilling off the latter, the mineral oil is left in a pure state.   L. DE K.

Partial Decomposition of the Constituents of Beer by Ebullition, and its Effect on the Estimation of Carbonic Anhydride and on the Detection of Sulphurous Acid. By H. ELION (*Rec. Trav. Chim.*, **12**, 255—261).—Among methods for the estimation of carbonic anhydride in beer, may be mentioned that of Schwackhöfer, improved by Langer and Schultze (*Zeit. ges. Brauw.*, 1879, 369). The method consists in driving out the carbonic anhydride with a current of air, but the last-named chemists contend that it is only possible to eliminate the last traces of carbonic anhydride by maintaining the liquid in ebullition for some time. The author ascribes the increased amount of carbonic anhydride found by prolonging the boiling to the decomposition of certain constituents of the beer.

Prior has shown (*Allg. Zeit. Bierbrau. u. Malzfab.*, 1891, 1281) that when hops are boiled with water, as in the process for detecting sulphurous acid, a small quantity of hydrogen sulphide is evolved, which complicates the process.

The author's results show that 5—10 minutes' ebullition is sufficient to eliminate all the carbonic anhydride from beer.

A. R. L.

Detection and Estimation of Alkyl Groups attached to Nitrogen. By J. HERZIG and H. MEYER (*Ber.*, **27**, 319—320).—It is found that the alkyliodide compounds of pyridine and quinoline decompose into base and alkylic iodide when heated, and that the hydriodides of bases which contain alkyl groups attached to the nitrogen atom behave in a similar manner. It is thus possible to estimate these groups by a modification of Zeisel's method.

No details of the process are given, as the method is still under investigation.

C. F. B.

Rosaniline Hydrochloride as a Reagent for the Detection of Mineral Acids in Vinegar. By G. GRIGGI (*Chem. Centr.*, 1893, ii, 1033; from *Chem. Zeit.*, **17**, Rep., 276).—1 c.c. of the vinegar to be tested is placed in a flat porcelain basin, and a drop of an alcoholic solution of magenta (25 grams magenta in 100 c.c. of 90 per cent. alcohol) added. If only acetic acid is present, the colour is slightly intensified, but otherwise unchanged. In the presence of 1 per cent. or more of mineral acid, the reddish-violet colour is changed to a dirty yellow.

L. T. T.

Estimation of Formic Acid. By A. LIEBEN (*Monatsh.*, **14**, 746—754).—Formic acid is easily and accurately estimated by titration with standard potassium permangante solution in the presence of sodium carbonate. The reaction takes place according to the equation $3KCHO_2 + 2KMnO_4 = 2MnO_2 + 2K_2CO_3 + KHCO_3 + H_2O$. An excess of sodium carbonate is without influence on the estimation, and if the solution is heated on the water bath, the manganese dioxide rapidly settles.

The author has examined the method devised by Scala (*Gazzetta*, **20**, 393), which is based on the reduction of mercuric chloride to mercurous chloride. An accurate determination of formic acid is obtained by this method only when 5·6 times the theoretical quantity of mercuric chloride is employed and the mixture is heated at least 6—8 hours on the water bath.

E. C. R.

Colour Reactions of Amines and Aldehydes without addition of Acids. By E. NICKEL (*Chem. Zeit.*, **17**, 1413).—Salts of aromatic amines, particularly those of aniline, give colour reactions with aldehydes. The author found, however, that the alcoholic solutions of the free bases also give colorations with some of the aldehydes. Experiments were made with the following amines—Aniline, ortho- and para-toluidine, α- and β-naphthylamine, and piperidine; also with the following aldehydes—Anisaldehyde, salicylaldehyde, para-hydroxybenzaldehyde, piperonal, and vanillin.

Excepting piperidine, all these amines give, in presence of acids, plain yellow colorations with the aldehydes. Without the presence of acids, the author could not get a colour by means of α-naphthyl-amine except with salicylaldehyde. The reaction of amines with hydroxyaldehydes or their derivatives is also different in the absence of acids. Aldehydes which contain a hydroxyl group, ortho- and para-hydroxybenzaldehyde, for instance, give, however, a yellow color-ation without the addition of acid, although not so strongly and quickly as with acid. But aldehydes, such as anisaldehyde and piperonal, which contain alkyloxy-groups, do not give the reaction without addi-tion of an acid.

Piperidine, which does not belong to the aromatic series and does not contain the group NH_2, but the imide group NH, behaves dif-ferently from the other amines. In the free state, it gives yellow colorations with salicylaldehyde or vanillin, which are destroyed by the addition of an acid. But with lignin, which is related to the alde-hydes, it gives a reaction, even in the presence of sulphuric acid.

L. DE K.

General and Physical Chemistry.

Refractive Powers of some Organic Phosphorus Compounds.
By F. Zecchini (*Gazzetta*, **24**, i, 34—42); compare Abstr., 1893,
ii, 353).—The author has determined the refraction constants of a
number of organic phosphorus compounds for the lines D and Hα.
The results obtained for the former ray are summarised in the follow-
ing table, and are each the mean results of several determinations
made under varied conditions.

Substance.	Temp.	$P\dfrac{\mu_D - 1}{d}$.	$P\dfrac{\mu_D{}^2 - 1}{d(\mu_D{}^2 + 2)}$.	Atomic refraction of phosphorus.	
				From μ_D	From $\mu_D{}^2$.
PPhCl₂	5·8— 7·0°	81·10	46·17	17·47	8·79
PPh₃	4·8— 6·9	156·75	87·94	26·16	11·79
P(OEt)₃	7·4—27·0	63·34	38·30	5·98	2·97
PO(OEt)₃	5·7—28·1	69·09	41·79	7·50	4·17
P(OEt)Cl₂	12·4—24·5	53·62	31·87	14·10	8·10
POPh(OH)₂	—	60·07	35 61	5·07	2 81

The values given for triphenylphosphine were obtained in 7—11
per cent. benzene solutions. Two determinations of the constants for
ethoxyphosphorous chloride were made with the pure substance, and
one with an 8 per cent. benzene solution; slightly higher results were
obtained in the latter case. The high atomic refraction of phosphorus
in triphenylphosphine is analogous to that previously observed by the
author with aromatic bases (this vol., ii, 2). The atomic refraction
of the phosphorus in phenylphosphorous chloride (17·47 for *n*) is
somewhat greater than that in phosphorous chloride (14·89 for *n*).

W. J. P.

Photochemical Action in Solutions. By M. Roloff (*Zeit.
physikal. Chem.*, **13**, 327—365).—The action of light on Eder's solu-
tion, that is, a mixture of solutions of mercuric chloride and ammo-
nium oxalate, is first considered. The presence of a double salt is
indicated by experiments on the alteration of the boiling point of
water by the addition of the two constituents singly and together.
The action of light on the solution causes the formation of mercurous
chloride, and the amount so formed is determined under various
conditions. The addition of substances which cause an increase in
the dissociation causes an increase in the quantity of mercurous
chloride formed and *vice versâ*. The author therefore concludes that
the undissociated molecules play no important part in the reaction.
As the acceleration of the action is most marked by an increase in

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the number of Hg and C_2O_4 ions, the reaction is considered to be due to these, that is—

$$2\overset{++}{Hg} + \overset{--}{C_2O_4} = 2Hg + 2CO_2.$$
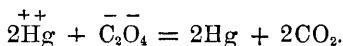
The mercury so formed then produces mercurous chloride by its action on the mercuric salt. As a photometric liquid, the solution is, however, subject to the disadvantages that it is relatively more sensitive in dilute than in strong solution, and that the carbonic anhydride formed by the reaction increases the sensitiveness.

The author then shows the probable existence of a compound, KBr_3, in a solution of bromine in potassium bromide solution, and examines next the action of bromine on oxalic acid—(1) in the dark ; (2) under influence of light. In the first case the reaction velocity was found to decrease rapidly with the time. As potassium bromide is formed in the reaction, the decrease is probably due to the formation of the salt KBr_3, and hence the removal of some of the bromine. The ratio of the reaction velocities in light and in the dark was found to increase greatly with the time. The ratio was also increased by the addition of potassium bromide, and in this case did not vary with the time. As before, increase in the number of ions caused an increase in both cases in the velocity of the reaction. The author concludes, therefore, that the influence of light in this case is due to an increase in the activity of the Br and C_2O_4 ions, and also to a raising of the activity of the Br_3 group.   L. M. J.

Electrodes for Resistance Determinations in Electrolytes. By F. KOHLRAUSCH (*Ann. Phys. Chem.*, [2], **51**, 346—350).—The author describes various forms of plane and cylindrical platinised platinum electrodes for dipping into liquids whose resistance is to be determined. One of the principal features of these electrodes is that the connections are made through double capillary glass tubes of 1·5 mm. bore.   J. W.

Electrical Conductivity of Gases. By F. BRAUN (*Zeit. physikal. Chem.*, **13**, 155—162).—A number of different cases were investigated :—

(1.) Compound gases at the moment of formation. The only cases studied were mixtures of (1) nitric oxide and air ; (2) chlorine and hydrogen, which were caused to unite by the influence of heat or diffused daylight. A Leyden jar battery of about 4000 volts E.M.F. was employed. No conduction was observable.

(2.) Gases during the time of explosion. A mixture of carbonic oxide and oxygen was employed, and a current from 7 to 20 small Grove cells was employed ; in this case, there appeared to be undoubted conduction through the exploding gas.

(3.) Gases heated to high temperatures. The gases were heated in porcelain tubes to about 1000—1200°, and the current used was that from a Leclanché cell. Ammonium chloride and cadmium iodide conducted well ; ammonia, iodine, and hydrogen chloride conducted, as did to a less extent hydrogen iodide, hydrogen bromide,

and probably mercuric oxide. No conduction was observed in the cases of carbonic anhydride, water, and nitric peroxide.

The paper closes with a short discussion of the electric charges of flames, which the author considers to be due to a separation of positive and negative ions.

The results in general confirm the experiments of De Hemptinne (Abstr., 1893, ii, 563). L. M. J.

Laws of Galvanic Polarisation and Electrolysis. By O. WIEDEBURG (*Ann. Phys. Chem.*, [2], **51**, 302—345).—The author seeks to give a consistent exposition of the phenomena of galvanic polarisation on the following fundamental assumptions. The ions are driven by the active electromotive force towards the two electrodes, where they collect and generate new breaks in the potential, which, acting against the original electromotive force, regulate the current according to Ohm's law. All the ions that reach the electrodes, however, are not electrically active, but only a small proportion of them, the rest being neutralised, losing their ionic character, and contributing nothing to the sudden difference of potential. There is a limit to the gathering of the ions at the electrodes, and the relative amount which collects at any instant is smaller, the nearer the amount already collected is to the limit, being proportional to the difference between the limiting and actual values at the instant considered. J. W.

Minimum Electromotive Force required to decompose Electrolytes. By M. LE BLANC (*Compt. rend.*, **118**, 411—412) and BERTHELOT (*ibid.*, 412—415).—Le Blanc points out that in 1891 (Abstr., 1891, 1405) he obtained results identical with those of Nourisson (this vol., ii, 178). Berthelot considers that both Le Blanc and Nourisson have only confirmed the conclusion at which he arrived in 1882 (*Ann. Chim. Phys.*, [5], **27**, 88), namely, that the minimum electromotive force required to decompose an electrolyte is the sum of the heat absorbed by the separation of the acid from the base in dilute solutions, and the heat of decomposition into oxygen and hydrogen of the water by which the acid and base are dissolved, provided that the acid and base are neither oxidised nor reduced and that the electrodes are not attacked. This result is independent of any theory of dissociation into ions. Berthelot points out that the numerical values obtained by himself, Le Blanc, and Nourisson respectively, are practically identical. C. H. B.

Fusibility of Isomorphous Mixtures of some Double Carbonates. By H. LE CHATELIER (*Compt. rend.*, **118**, 415—418).— Potassium carbonate and sodium carbonate, when fused with calcium, barium, or strontium carbonate, readily yield crystalline isomorphous double salts of the general formula M'_2O, $M''O$, $2CO_2$. They cleave easily, and when the plates are examined with convergent polarised light they are found to be negatively uniaxial, with the axis perpendicular to the plane of cleavage. They do not alter when exposed to

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air, but decompose when heated above their melting points, the barium compounds being less stable than those which contain calcium.

Lithium carbonate will not combine with carbonates of the calcium group, but, on the other hand, forms double compounds with the alkali carbonates.

The following table shows the points of solidification of various mixtures, the numbers indicating the molecular proportions of each salt present in the mixture.

Na_2CO_3	1	1	1	—	—	1	1
K_2CO_3	—	—	—	1	1	—	—
$CaCO_3$	1	—	—	1	—	0·5	0·5
$SrCO_3$	—	1	—	—	—	0·5	—
$BaCO_3$	—	—	1	—	1	—	0·5
Temperature of solidification.	790°	750°	740°	790°	800°	720°	660°

Na_2CO_3	1	—	0·5	0·5	0·5
K_2CO_3	—	1	0·5	0·5	0·5
$CaCO_3$	—	0·5	1	—	0·5
$SrCO_3$	0·5	—	—	—	—
$BaCO_3$	0·5	0·5	—	1	0·5
Temperature of solidification.	720°	755°	760°	780°	690°

The connection between the melting point and the composition can be represented by a triangular surface in the case of ternary mixtures, and by a square surface in the case of quaternary mixtures.

These results and those previously obtained (this vol., ii, 179) show that in all cases where the isomorphism can be decisively ascertained, the curves and the surfaces are perfectly continuous, and show no angular points.

When the temperature of the fused mixture remains constant during solidification, the crystals have the same composition as the mother liquor in which they are formed. Such mixtures in the case of alloys have been termed eutectic mixtures by Guthrie. Such mixtures show the minimum melting point, and for any pair of solids there is always one eutectic mixture. The same properties would seem to belong to the whole series of isomorphous compounds, the heat of formation of which is nil. In this case, the curve of the melting point is a right line connecting the melting points of the two constituents. With other mixtures, the melting point becomes lower and lower as crystallisation proceeds, the difference in composition between the crystals and the still liquid part being such that the composition of the latter tends towards the eutectic mixture, and finally reaches it.

C. H. B.

Thermal Expansion and Compressibility of Solutions. By G. TAMMANN (*Zeit. physikal. Chem.*, **13**, 174—186).—The author observes that the thermodynamic surface of a solution approximately coincides with that of its solvent if for the former the zero of pressure be taken, not as 1 atmosphere, but as a higher value, Δk. This is expressed otherwise, thus if $\phi(p.v.t.) = 0$ represent the thermo-

dynamic surface of the solvent, $\phi(p + \Delta k, v.t) = 0$ represents that of the solution. In the simplest case Δk is independent of t. The section of the surface by planes perpendicular to the axis of pressure gives the isobars of the liquid. In the case of water, the isobars for high pressures fall above those for low, the reverse holding for other liquids. Corresponding with this is the fact that in solutions of the same substance in water, the isobars for high concentrations lie above those for low. A number of solutions are then compared, the data being obtained from the experiments of Marignac and Amagat. The pressures at which water has a similar expansion is found for solutions at five concentrations, and at four different temperatures in the cases of hydrogen chloride, sodium chloride and sulphate, and cane-sugar; the numbers obtained show that Δk is approximately proportional to the concentration, and increases slightly with the temperature. Calculations are also made from the determinations of Amagat on the lowering of the temperature of maximum density of water by pressure, and of Despretz and Rosetti on the similar lowering by solution of salts; the numbers for Δk agree satisfactorily with those previously obtained. The isobars of water cut one another at about 125—130°, hence, at this temperature, the isobars of salts of different concentration should cut each other and that of water; this is the case with sodium carbonate, but in other cases, owing to the increase of Δk with temperature, the temperature is lower than this. Also the coefficient of expansion of water at about 55° is the same for all pressures below 1000 atmospheres, and is equal to that of solutions at the same temperature, but for liquids in which Δk varies the point is slightly different.

The *isotherms* are next compared, and comparisons made by means of Tait's researches on the compressibility of salt solutions and of Amagat on the compressibility of water show satisfactory agreement.   L. M. J.

Electrolytic Decomposition of Water. By M. Le Blanc (*Zeit. physikal. Chem.*, **13**, 161—173).—The author in this paper upholds the view of the primary decomposition of water, and replies to the objections brought forward by Arrhenius (Abstr., 1893, ii, 441). The increase in the electrolytic decomposition of water by the addition of an electrolyte is explained, not by an increase in the degree of dissociation of the water, but in the capability of ion formation. He also explains the fact that hydrogen is not immediately liberated during the electrolysis of an alkali salt with a mercury cathode, by stating that the potassium ions give up their electricity to the mercury more readily than the hydrogen ions. That hydrogen ions are present in water is shown also by the fact that potassium reacts readily with water and not with paraffin. In the case of solution of various metallic cyanides in potassium cyanides, he points out that cadmium is easily separable, but platinum scarcely so, which is hard to explain on a secondary decomposition hypothesis, unless the electro-deposited platinum were soluble in potassium cyanide; this, however, he proves experimentally is not the case. He finally points out that the primary decomposition theory has the advantage of simplicity.
                                                        L. M. J.

Hypothesis of Coloration of the Ions. By G. MAGNANINI (*Gazzetta*, **24**, i, 48—56).— Violuric acid has an affinity constant $K = 0.00272$. In an aqueous solution containing 1 gram-mol. of the acid in 256 litres, about 8 per cent. of the molecules present are dissociated into their ions; such a solution is colourless, or has, at most, a very slight yellow tint, and the ions, according to Ostwald's hypothesis (Abstr., 1892, 1137), are therefore practically colourless. The pure potassium, sodium, and ammonium salts of violuric acid have different colours when solid, but their aqueous solutions have the same red tint. The author has measured the coefficient of absorption of these three salts for aqueous solutions containing 1 gram-mol. in 50 and 100 litres, and confirms his previous observation (Abstr., 1892, 757; 1893, ii, 510) that the absorption coefficient is directly proportional to the number of gram-mols. of salt in solution. Further, the addition of a quantity of potassium nitrate to the solution, sufficient to diminish the electrolytic dissociation by 25 per cent. has no effect on the absorption.

Ostwald's hypothesis that, in an electrolyte, the dissociated part has a different colour from that of the non-dissociated part is therefore opposed to facts. W. J. P.

Stochiometry of the Ions. By G. BREDIG (*Zeit. physikal Chem.*, **13**, 191—288).—The author gives, firstly, a brief review of the position of our knowledge with regard to the ion migration. A table is next given for the conversion of the conductivity of a solution at various degrees of dilution into that at infinite dilution; this depends only on the product of the valencies of the ions, and not on their nature, and its validity is shown by a comparison of calculated numbers with those obtained by Kohlrausch. The exceptions, for instance, in magnesium salts, are referred chiefly to hydrolytic decomposition and to differences in the mode of ion formation. To the available data the author adds a large number of conductivity numbers obtained from his own experiments, more especially in the case of organic bases, the conductivity of about 150 substances having been determined by means of an alternating current and telephone; aqueous solutions of different strengths were employed in most cases, and the results carried to infinite dilution. About 300 different substances were thus available for discussion. As follows theoretically, the difference $\mu_{1024} - \mu_{32}$ was approximately constant. Such substances as aniline chloride, which are partially decomposed in aqueous solution, were examined in a solution of the base itself. From these data, using the value of Nernst and Loeb for the velocity of the silver ion ($a_{Ag} = 59.1$), the velocities of about 300 ions are calculated, and then, by means of the above-mentioned table, the conductivity of the substance at μ_{128}; in almost all cases the agreement between these numbers and those found experimentally, is very good. The ion velocities are in all cases given in mercury units; so that for conversion into C.G.S. units they should be multiplied by 110×10^{-7}. From the results obtained the author points out the following relations.

The velocity of the elementary ions is a periodic function of the

atomic weight, the curve being also very closely analogous to that for internal friction.

In complex ions, the velocity is largely an additive property; isomeric ions of analogous constitution have equal velocities; and to a continuous additive change in the composition of the ion corresponds a continuous, but decreasing, change in the velocity.

In general, a retarding effect is produced by the replacement (i) of H by Cl, Br, I, Me, NH_2, or NO_2; (ii) of any element by an analogous element of higher molecular weight (exc. O and S), of NH_3 by H_2O; of $(CN)_6$ by $(C_2O_4)_3$, by the change of amines into acids; of sulphonic acids into carboxylic acids, acids into cyanamides, dicarboxylic into monocarboxylic acids, and by monamines into diamines.

The additive effect is, however, largely influenced by constitution. Thus in metamerides the velocity increases with the symmetry of the ion, especially with increase in the number of C—N unions.

To the paper is also added an addendum showing the accordance of the author's numbers with those recently published by Kohlrausch (this vol., ii, 79).   L. M. J.

Non-electrolytic Dissociation in Solutions. By M. WILDERMANN (*Ber.*, **26**, 2881—2897).—The author has in a previous paper (Abstr., 1893, ii, 509) advanced the view that in solutions the dissolved substance is contained in the condition of complex (higher) and simple (lower) molecules and of the products of dissociation of these, the dissociation of the higher molecules being non-electrolytic, and that of the lower molecules being electrolytic in character. This view evidently agrees with that of Arrhenius in assuming in electrolytes the existence of simple molecules and their ions, but goes further, and adds to these the presence of higher molecules and their products of dissociation in smaller or greater quantity. It is likewise maintained that all dissolved substances in all solvents whatsoever and at all strengths of the solution, undergo electrolytic dissociation.

The electrical conductivity of solutions was considered in the former paper (*loc. cit.*), and the views above given were found to afford an explanation of facts which the theory of electrolytic dissociation alone was incapable of explaining. In the present paper, the depression of the freezing point is considered, and here also the assumption of the existence of complex molecules and non-electrolytic dissociation is found to afford a general explanation of the observed facts.   H. C.

Applications of Raoult's Law at the Boiling Point of Solutions. By O. ŠULE (*Ber.*, **27**, 594—595; compare Abstr., 1893, ii, 406).—A solution of rhamnose in ethylic alcohol is lævorotatory, whilst in isopropylic alcohol or in water it is dextrorotatory. Further, the molecular weight of rhamnose as determined ebullioscopically, is too great in its solutions in methylic and in ethylic alcohol, but normal in isopropylic alcohol and in water. But all the lower alcohols behave in the same way ebullioscopically with regard to such a substance as water; hence the differences observed above must have their source in the rhamnose. Probably they are caused by the formation of

rhamnose alkyl oxides which are stable in alcoholic solution; it is known that rhamnose hydrate, for example, is decomposed by amylic alcohol, water distilling over; and, in fact, the ethyl rhamnoside (rhamnose ethoxide) of Fischer was found to be lævorotatory in alcoholic solution.   C. F. B.

Exact Method for the Determination of the Reduction of the Freezing Point. By E. H. LOOMIS (*Ann. Phys. Chem.*, [2], **51**, 500—523) and by F. KOHLRAUSCH (*ibid.*, 524—528).—Loomis' method for cryoscopic determinations is that described in a former paper (Abstr., 1893, ii, 261), and details of experiments with the substances mentioned in that communication are given. In the case of sodium chloride, the numbers obtained are in excellent agreement with those of Jones, and differ from those of Pickering in showing no breaks in the continuity of the freezing-point curve.

Kohlrausch draws attention to the fact that the close agreement between the results of Loomis and of Jones in the case of sodium chloride does not hold for the other substances examined by the two observers. Possible sources of error in Jones' results are suggested, and particular attention is drawn to the wavy character of some of his freezing-point curves, a point which Pickering (Trans., 1894, 293) has also commented on.   H. C.

Proportionality between the Reduction of the Freezing Point and the Osmotic Pressure. By S. ARRHENIUS (*Ann. Phys. Chem.*, [2], **51**, 493—499).—The proportionality which the author maintains exists between the reduction of the freezing point and the osmotic pressure has recently been called in question by Dieterici, who bases his arguments upon observations of W. Fischer. It is shown that the untrustworthiness of Fischer's experimental work invalidates Dieterici's conclusions, and that, substituting observations by Juhlin, excellent agreement with the author's theory is obtained.
                                                        H. C.

Nature of Osmotic Pressure. By G. MAGNANINI (*Gazzetta*, **24**, i, 81—90).—The author replies to a paper by Naccari, in which the latter defends his experiments on the osmotic pressure of sugar solutions; the fallacy of the experiment has been previously pointed out by the author, by Le Blanc, and in a note to the abstract of Naccari's first paper on the subject (Abstr., 1893, ii, 513).   W. J. P.

Cryoscopy of the Hydrate H_2SO_4,H_2O. By R. LESPIEAU (*Bull. Soc. Chim.*, [3], **11**, 71—76).—A large quantity of the monohydrate of sulphuric acid was fractionally crystallised until the melting point rose to, and remained stationary at, 8·53°, a temperature identical with that observed by Pickering. The extreme variations noted in the temperature of a mixture of crystals and liquid during 48 hours was 0·04°. The only experimental difficulty is that due to superfusion, crystallisation being difficult to induce and tedious to carry out.

The constants in the equation $Mx/p = cx + K$, where $x =$ lowering of freezing point, $p =$ percentage of dissolved substance, $M =$ mole-

cular weight of dissolved substance, a = constant for solid, K = constant for solvent, were determined for acetic, pyruvic, and uric acids.

$$a = 1\cdot2, -2\cdot7, 13\cdot3,$$
$$K = 48\cdot1, 47\cdot5, 48\cdot0.$$

K may, therefore, be taken as 48.

The value of K, calculated from the latent heat of fusion, is $49\cdot5$, taking Berthelot's value, $31\cdot7$ Cal., and $39\cdot3$, taking Pickering's value, $39\cdot9$ Cal.

Thus, from the cryoscopic point of view, this molecular compound behaves as an individual.   JN. W.

Degree of Affinity of Some Insoluble Mineral Bases. By J. MIJERS (*Rec. Trav. Chim.*, **12**, 315—329).—The relative affinities of certain insoluble mineral bases were determined from the rate of action of the insoluble base silver oxide on solutions of their nitrates. Decinormal solutions were taken, and most of the experiments were carried out at the boiling points of these solutions. The nitrates of zinc, copper, lead, and cadmium were first examined. Some difficulty was experienced with the lead and cadmium solutions, owing to the formation of basic salts, but it was eventually found that the order of affinity (basicity) of the hydroxides is as follows, beginning with the weakest :—$Cu(OH)_2$, $Zn(OH)_2$, $Cd(OH)_2$, $Pb(OH)_2$. Experiments with magne ium nitrate proved unsuccessful, owing to secondary reaction and rmation of a compound, $Mg(OAg)_2$, which is deposited in the form of light yellow needles upon the sides of the vessel containing the solution. Calcium and barium nitrates behave in a similar manner. The author finds, however, that silver nitrate is completely decomposed by magnesium oxide at the ordinary temperature. The affinities observed are not, as might be expected, proportional to the relative amounts of electrolytic dissociation in the nitrates examined, and in so far contradict the accepted view of the identity of chemically and electrically determined affinities.

       H. C.

Affinity Coefficients of Bases. By G. BREDIG (*Zeit. physikal. Chem.*, **13**, 288—326).—A large number of affinity coefficients were determined, chiefly of bases the conductivity of whose chlorides the author had previously determined (this vol., ii, 226). The measurements were all made electrolytically by use of the telephone and alternating current. The values for $\mu\infty$ were calculated from the previously obtained numbers for the ion velocities, using the value $a'_{\text{OH}} = 167$. The affinity coefficient is given by the equation

$$k = \frac{m^2}{v(1-m)},$$

where m is the degree of dissociation = $\mu\infty/\mu_v$, and v is the volume of solution per gram molecular weight.

The results show that the quaternary organic bases are the strongest and the tertiary the weakest. The bases of phosphorus, arsenic, antimony, sulphur, and tellurium are very strong; those of

tin and mercury very weak. In metameric diamines the base is stronger the further removed are the amido-groups.

A number of very weak bases were examined in solutions of the hydrochloride, and the value k_3/k_4 determined; that is, the strength of the base referred to that of water. The ratio multiplied by $2\cdot29 \times 10^{-16}$ gives the affinity constant of the base.

The author upholds the accuracy of the electrolytic method, more especially with regard to objections raised against it by Lellmann (Abstr., 1892, 1269; 1893, ii, 407).   L. M. J.

Affinity Coefficients of Organic Bases. By E. LELLMANN and A. LIEBMANN (*Annalen,* **278,** 141—152).—Continuing the experiments of Lellmann and Görtz on aniline (Abstr., 1893, ii, 407), the authors find that this base has a fixed value for its affinity coefficient which varies, however, under certain influences. It is hardly probable that all these influences have been ascertained, but the authors have qualitatively proved the effect of agitating the solution during the experiment, and also the action of magnetism. They intend to repeat their observations quantitatively. It is noteworthy that the influence of agitating the solution raises the affinity coefficient, whilst the influence of magnetism lowers it.   A. R. L.

Affinity Coefficients of Acids. By E. LELLMANN and A. LIEB-MANN (*Annalen,* **278,** 152—173).—It has been shown by Lellmann and Schliemann (Abstr., 1893, ii, 408) that determinations of the affinity coefficients of acids in aqueous solution by the spectrophotometric method give results incompatible with Guldberg and Waage's law. Abnormal results are also obtained when 96 per cent. alcohol is used as the solvent, but the values, unlike those obtained in aqueous solution, increase with the concentration. Results quite in accord with the law of mass action are obtained when 50 per cent. aqueous acetone is used as the solvent.

Numerous determinations of the affinity coefficient of phenylacetic acid are recorded, the barium salt, as before, being examined. Great differences in the values were observed, the causes of which are unknown, but may, perhaps, be the same as suggested in the case of aniline (last abstract). The authors have made a series of determinations of the electrical conductivity of phenylacetic acid and its barium salt, and, comparing their results with the values obtained by the spectrophotometric method, they conclude that there is no proportionality between electrical conductivity (dissociation) and chemical activity. They also reply to the criticisms of Nernst (Abstr., 1893, i, 449).   A. R. L.

Laboratory Apparatus. By A. BIDET (*Compt. rend.,* **118,** 473—480).—*A constant level siphon* (Fig. 1) is obtained by attaching a lateral tube, O' S, to an S tube a little above the lower bend. The lower branch is placed in the vessel in which the constant level is to be maintained, and the water is brought in through the upper vertical branch, A. When the level of the liquid in the vessel falls below the

lower bend, the siphon acts in the direction BO ; if it rises higher, the siphon acts in the direction BS.

The *safety tube* (Fig. 2) allows of the introduction of an acid, whilst any gas that is evolved escapes through the lateral tube. If the pressure inside the vessel becomes high, the liquid in the cylindrical bulb is driven up into the funnel and the gas escapes through the bent tube without projecting the liquid from the funnel ; when the pressure falls, the liquid runs back from the funnel into the bulb.
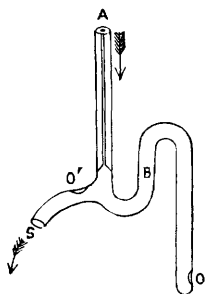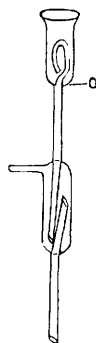
Fig. 1.   Fig. 2.

Condenser with Internal Circulation.—A wide tube, closed at one end, is fused into the lower end of a wide condenser tube, so that a narrow, annular space is left between them. The inner tube is fitted with a cork carrying two tubes, one for the entrance, the other for the exit of cold water. One end of the outer tube is connected with the distilling flask and the lower end with the receiver. If necessary, a third tube may be added, giving an outer circulation of water as well.

Commutator for Condensers (Fig. 3).—This consists of an external
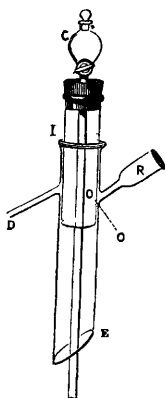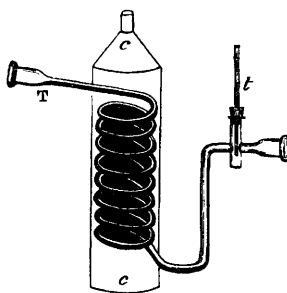
Fig. 3.   Fig. 4.

tube, E, carrying two tubulures, one of which, R, communicates with
the reflux condenser, whilst the other, D, can be attached to a descend-
ing condenser. The internal tube, I, turns in such a manner that
the aperture, O, can be brought opposite either R or D. The apparatus
is attached by means of a cork to the vessel containing the liquid,
and the vapour can be sent into either condenser by altering the
position of the aperture O. A funnel, thermometer, &c., can be passed
through the inner tube, as shown in the figure.

A convenient *superheater* (Fig. 4) for vapours can be constructed
of a helix of copper tube, with a core of metallic gauze, the whole
being surrounded by a metal cylinder with an open conical top. The
flame of a Bunsen burner is allowed to play on the gauze in the centre
of the helix, and it is easy to maintain a temperature of 300°. The
temperature of the issuing vapour is indicated by the thermometer,
t, placed in the vertical side tube.   C. H. B.

Lecture Experiment: Electrolysis of Hydrochloric acid. By
L. MEYER (*Ber.*, **27**, 850—853).—The method usually adopted for
the electrolysis of hydrochloric acid as a lecture experiment invari-
ably yields less chlorine than hydrogen, even when the liquid has
been previously saturated with chlorine. This is due to the fact that
in the ordinary form of apparatus (Hofmann's) the chlorine is col-
lected under a gradually increasing pressure, and has to pass up
through a long column of the acid, which dissolves more and more of
the gas as the experiment proceeds and the pressure on the chlorine
increases. This is largely prevented in the apparatus described by
the author, in which the chlorine does not pass through the acid, but
only comes in contact with its surface. This is effected by collecting
the gases in tubes which are connected by ground joints with the two
limbs of the ⊢-shaped apparatus containing the electrodes, the gas
entering at the top of the collecting tubes.   A. H.

Inorganic Chemistry.

Hydrates of Hydrogen Bromide. By S. U. PICKERING (*Phil. Mag.*, [5], **36**, 111).—A series of density determinations were made with solutions containing from 65 per cent. of hydrogen bromide downwards, and the results examined graphically. They gave indications of two not very well marked breaks at strengths corresponding with a tri- and tetra-hydrate. On making a series of freezing-point determinations, both these hydrates were isolated in the crystalline condition, the former melting at −48°, the latter at −55·8°. With the exception of the previously known di-hydrate, no other hydrate was isolated. There are some grounds, however, for regarding the existence of a pentahydrate as probable, although solutions of about that strength did not solidify at −80°.

For the hydrates of hydrogen chloride see *Ber.*, **26**, 277, and also Proc., 1893, 45 ; for those of hydrogen iodide, together with a list of the various hydrates, isolated in the cases of the three haloïd acids, see this vol., ii, 11.   S. U. P.

Action of Dry Ammonia on Dry Carbonic Anhydride. By R. E. HUGHES and F. SODDY (*Chem. News*, **69**, 138—139).

—Ammonia, carefully dried by means of soda-lime, solid caustic soda, and ignited lime, and carbonic anhydride, carefully dried by means of sulphuric acid and phosphoric anhydride, are found not to react when mixed together.   D. A. L.

Preparation of Pure Potassium Iodate. By M. GRÖGER (*Zeit. angw. Chem.*, 1894, 13).

—40 grams of pure potassium permanganate is dissolved in 1 litre of hot water. 20 grams of potassium iodide, dissolved in a little water is added, and the whole heated in a boiling water bath for 20—30 minutes, when the excess of permanganate is reduced by the cautious addition of alcohol. The filtrate is acidified with acetic acid, and evaporated to about 50 c.c. The mother liquor is poured off, and the crystals of potassium iodate are washed with strong alcohol, and dried.   L. DE K.

Behaviour of Sodium Peroxide towards acids. By J. TAFEL (*Ber.*, **27**, 816—824).

—Sodium peroxide evolves oxygen when strongly heated or on treatment with water at ordinary temperatures. By the action of alcoholic hydrochloric acid at about 0°, a white powder is formed, which, after purification, undergoes decomposition at 100°, oxygen being evolved. This substance is a mixture, or a compound, of 2 mols. $NaCl$ and 1 mol. $NaO \cdot OH$. It decomposes gradually at the ordinary temperature, dissolves in ice-cold water without evolution of gas, and the solution has a strongly alkaline reaction. On acidifying with sulphuric acid, the solution reduces potassium permanganate at the ordinary temperature, oxygen being liberated ; on boiling the acid solution, it is decomposed somewhat slowly. On acidifying the alkaline solution with hydrochloric acid, instead of sulphuric acid, chlorine is evolved on heating, and potassium iodide is decomposed at the ordinary temperature. Sodium peroxide dissolves in alcoholic acetic acid, and a compound is deposited which resembles the preceding substance in appearance and general properties, but its aqueous solution is neutral. On heating the solid, oxygen and water are eliminated and sodium acetate remains ; the compound is, therefore, either sodium acetate with hydrogen peroxide, instead of water of crystallisation, or, more probably, a mixture of sodium acetate with the compound $NaO \cdot C_2H_3O_2$, the acetic derivative of the hydrate $NaO \cdot OH$. Failure to detect the formation of hypochlorous acid, or of sodium hypochlorite, by the action of alcoholic hydrochloric acid on the acetate, leads the author to suggest the formulæ, $O \vdots Na \cdot OH$ and $O \vdots Na \cdot OAc$, for the hydrate and acetate respectively. The consequences resulting from the assumption of a tervalent sodium atom will be considered subsequently. Full analytical details of the compounds are included in the paper.
                                                                            J. B. T.

Trihydrate of Lithium Iodide. By A. N. THIRSOFF (*J. Russ. Chem. Soc.*, **25**, 467—472).—The salt, $LiI,3H_2O$, first prepared by Rammelsberg, melts at 72°, and can be crystallised unchanged from absolute alcohol. At 120° it loses water slowly, 1 mol. being given up much more readily than the other two. J. W.

Lithium Fluoride. By C. POULENC (*Bull. Soc. Chim.*, [3], **11**, 15—17).—Lithium fluoride may be obtained in a crystalline form by fusing the amorphous compound with a mixture of potassium hydrogen fluoride and potassium chloride. On slowly cooling the melt, and washing away the flux with water, the fluoride is obtained as a mixture of regular octahedra and small, nacreous spangles derived from the latter. The spangles are alone formed if the potassium chloride is omitted from the flux.

Lithium fluoride is intermediate in character between the alkali fluorides and those of the alkaline earths. It is sparingly soluble in water, but insoluble in 95 per cent. alcohol. It is easily decomposed by nitric and sulphuric acids, but with difficulty by aqueous hydrochloric acid, although at a red heat it is completely decomposed by gaseous hydrogen chloride, and partially by steam. It does not form a fluorchloride. It melts at about 1000° in an atmosphere of hydrogen fluoride, and partially volatilises at 1100—1200°. Jn. W.

Action of Hydrogen on Cæsium Oxide. By N. BEKETOFF (*J. Russ., Chem. Soc.*, **25**, 433—434).—Anhydrous cæsium oxide, when brought into contact with hydrogen, at once darkens, with slow absorption of the gas. A trace of moisture serves to make the action recommence after it has ceased in dry hydrogen. According to the author, the action is expressed by the following equation:—
$$2Cs_2O + H_2 = 2Cs + CsOH.$$ J. W.

Silver Aurochloride. By F. HERRMANN (*Ber.*, **27**, 596—597).—This substance, $AgAuCl_4$, may be obtained by dissolving 4 parts of gold in aqua regia, evaporating the solution nearly to dryness, adding first a solution of 1 part of silver in dilute nitric acid, and then 10 parts of the strongest nitric acid, evaporating almost to dryness, and repeatedly adding very strong nitric acid to the residue, and evaporating it. It is thus obtained in lustrous, orange-red needles with yellow streak; it darkens in colour superficially when exposed to sunlight in moist air, decomposes when heated at about 230°, and is only slowly decomposed by water, but rapidly by dilute hydrochloric acid and by ammonia. C. F. B.

Composition of some Mortars. By O. REBUFATT (*Gazzetta*, **24**, i, 28—33).—The author has analysed a specimen of mortar taken from the base of some Roman pillars about 2,000 years old, at about 11·5 metres under the sea surface; a mortar about 20 years old, taken from a pier, was also examined. Both mortars are trachytic, and very similar in composition, the latter being represented by
$$5SiO_2,2—3Al_2O_3,1—2(CaO,MgO),10H_2O.$$
W. J. P.
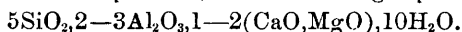
Scott's Cement. By G. GIORGIS (*Gazzetta*, **24**, i, 23—28).—The author is examining the "Scott's Cement" prepared by heating calcium sulphate with lime, but publishes no conclusions as to its nature in this preliminary note.   W. J. P.

Graphochemical Calculations, with especial Reference to Soda Lime Glasses. By E. NICKEL (*Zeit. physikal. Chem.*, **13**, 366—372) —A further application of the author's method of calculation. (Abstr., 1892, 1158, and 1893, ii, 119.)   L. M. J.

The Precipitation of Metals from Dilute Solutions. By F. MYLIUS and O. FROMM (*Ber.*, **27**, 630—651).—*A Wet Method of forming Metallic Alloys.*—*Silver-zinc* is obtained when a solution of silver sulphate is gradually added to water in which a zinc-plate is placed, the silver solution being added at such a rate that not more than 0·03 gram of silver is present per litre. No evolution of hydrogen is observed, and the product is precipitated as a black, amorphous mass, which is, however, sometimes contaminated with white silver crystals, especially if the solution is too strong. The product contains from 75·3—48·2 per cent. of silver and 24·7—51·8 per cent. of zinc. When rubbed with an agate rod. it acquires a white metallic lustre. When treated with concentrated silver nitrate, it yields white crystalline silver and zinc nitrate ; with strong acids, it yields silver, hydrogen, and a zinc salt. It precipitates copper and gold from their solutions. It is oxidised slowly by exposure to air, and with faintly acid hydrogen peroxide yields white silver. With bromine water, it yields white silver and silver bromide; and chromic acid converts it into zinc and silver chromates.

Copper-zinc is obtained in a similar way to the silver-zinc. A small quantity of hydrogen is evolved during the action, and a small quantity of basic zinc sulphate precipitated. It is a black, amorphous powder, containing from 59·4—50 per cent. of copper and 40·6—50 per cent. of zinc. When rubbed, it acquires a yellow metallic lustre, and is essentially a brass. It behaves like brass towards dilute acids. With concentrated copper solution, it forms crystalline copper and zinc sulphate, precipitates gold and silver from their solutions. and yields hydrogen and a residue of crystalline copper when treated with acids.

Gold-zinc, obtained in a similar way to the above, forms black, spongy flocks, containing equal weights of the two metals.

Those metals which, like platinum, iridium, and palladium, have a great affinity for zinc, are precipitated from their dilute solutions as black precipitates containing large quantities of zinc. Metals which have less affinity for zinc behave differently. A very dilute solution of lead chloride or acetate gives a grey precipitate which contains only 3—5 per cent. of zinc, a part of which is probably present as oxide. Tin and cadmium solutions behave in the same way.

Silver-cadmium is obtained as a black, spongy precipitate containing 54·4—35·2 per cent. of silver and 45·6—64·8 per cent. of cadmium. Under pressure it acquires a white, metallic lustre, and is similar to silver-zinc in chemical properties.

Copper-cadmium is obtained as a greyish-black, crystalline precipitate, and has the composition Cu_2Cd. When treated with concentrated hydrochloric acid, a violent evolution of hydrogen takes place, but the residual copper still contains a trace of cadmium.

Gold-cadmium is a lead-grey crystalline precipitate, having the composition $AuCd_3$. It remains unaltered by exposure to air, decomposes solutions of the noble metals, is scarcely acted on by dilute acids, and, when treated with concentrated hydrochloric acid, yields hydrogen, gold, and cadmium chloride. When heated, it is converted into gold-monocadmium $AuCd$ (Heycock and Neville, Trans., 1892, 906).

Cadmium precipitates the metals of the platinum group from dilute solution in a spongy form containing large quantities of cadmium. With dilute lead solutions, it gives a crystalline precipitate consisting of pure lead.

Copper-tin. A tin plate in contact with a very dilute neutral or acid copper solution becomes covered with a grey coating of crystals having a metallic lustre; the liquid at the same time becoming turbid, owing to the formation of a basic tin salt. The product has the composition Cu_3Sn; it is fairly stable towards acids, and is decomposed by hot concentrated hydrochloric acid with evolution of hydrogen, leaving a residue of red copper which, however, still contains tin. The authors point out that an alloy of the two metals of the composition Cu_3Sn has been shown to have the properties of a definite chemical compound (Laurie, Trans., 1888, 104, Riche, *Compt. rend.*, **55**; Mallet, *Fehling's Handwörterb.*, **3**, 1227; Lodge, *Phil. Trans.*, 1879; and Calvert and Johnson, *Phil. Trans.*, 1858).

Tin precipitates from dilute silver solutions a black compound containing a large quantity of tin; it is, however, very unstable, and contains also tin oxide. With dilute gold solutions, tin gives a dark precipitate which evolves hydrogen with concentrated hydrochloric acid. Gold-purple containing tin oxide is always formed at the same time. With platinum solutions, tin gives black and yellowish-brown precipitates.

From dilute copper solutions, lead precipitates a reddish-brown compound containing lead, which gives hydrogen when treated with hydrochloric or acetic acid. A plate of lead in dilute silver solution at first becomes covered with a dark film, but crystalline silver is very soon formed. *Gold-lead* is, however, easily formed, and is a deep black precipitate which gives hydrogen and gold when treated with acids. *Platinum-lead* is obtained as a crystalline precipitate; *Iridium-lead* is also easily obtained.

The authors were unable to separate an alloy by the action of copper on dilute silver solutions, as crystalline silver is precipitated at the same time. With gold solutions, they obtained a black, spongy compound containing copper, and a similar compound with platinum solutions. By the action of mercury on dilute silver solutions a beautiful crystalline amalgam is obtained. Iron acts on dilute neutral solutions of the metals with evolution of hydrogen, and alloys could not be obtained with copper, silver, or gold; with platinum solutions

however, a precipitate is obtained which contains iron, and evolves hydrogen when treated with hydrochloric acid.

The alloys described above are most easily prepared by shaking the positive metal in the form of powder with a solution of the negative metal. They undergo double decomposition like other insoluble chemical compounds; thus gold-zinc, when shaken with a cadmium solution, yields gold-cadmium and a zinc salt; and the compound Cu_3Zn, obtained by shaking zinc-dust with a solution of copper sulphate, when shaken with a solution of tin chloride yields copper-tin, Cu_3Sn, and zinc chloride.

The black metallic precipitates obtained by electro-deposition are not identical with the above, although they are very similar. The black metallic deposit obtained from silver solutions acts in the same way as zinc-silver towards concentrated silver solution, dilute acids, and oxidising agents. When silver is deposited from a dilute, faintly acid, sulphate solution on a wire cathode with a large current density, a black flocculent substance is obtained which is suddenly converted into white crystalline silver with evolution of hydrogen. Black silver deposited from a neutral solution contains no hydrogen, or only a very minute quantity. Platinum, cadmium, and zinc can also be deposited in a black porous condition, but lead cannot.

The authors have examined the behaviour of copper hydride under certain conditions. With a solution of potassium cyanide, it gives cuprous cyanide, potassium hydroxide, and hydrogen; with copper sulphate, it gives copper and free sulphuric acid. It may be cautiously heated to 140°, without completely decomposing. It cannot be prepared by the action of zinc on an acid solution of copper sulphate, the compound obtained under these conditions being copper-zinc (*Schoor. Arch. Néerland*, **12**, 96). The black precipitate formed at the zinc pole of a Daniell's cell is also copper-zinc, and when the cell is exhausted copper-zinc is also deposited at the copper pole. The authors were unable to obtain copper hydride by electro-deposition.

E. C. R.

Allotropic Changes of Iron under the Influence of Heat. By G. CHARPY (*Compt. rend.*, **118**, 418—421).—When iron is in the α-condition it shows a rectilinear break in the curve representing the elongation as a function of the load, but the modification β shows no such break. The relative proportions of α and β in a given bar can be estimated by comparing the length of the rectilinear break in its curve with that of a bar which has been completely converted into the α-modification. The author has applied this fact to the investigation of the condition of iron that has been heated to various temperatures in an electric muffle, and cooled by suddenly immersing it in a cold liquid.

The results obtained show that the allotropic modification of iron takes place spontaneously at a sufficiently high temperature, and can be made permanent by sudden cooling; it therefore plays an important part in the operation of tempering. The transformation takes place more quickly, the higher the temperature; with steel containing 0·8 per cent. of carbon, the change does not begin after heating for an hour at 700°, or for five minutes at 750°, but it is complete after

heating for 30 minutes at 750°, or for five minutes at 800°. Other steels yield similar results, and it follows that in metallurgical operations it is necessary to take into account not only the temperature, but also the time during which the temperature is maintained.

When iron is tempered, it undergoes a change which can also be produced by deformation in the cold, but there is no evidence to show whether this change is the cause of the hardening.   C. H. B.

Higher Oxides of Nickel. By E. D. CAMPBELL and P. F. TROW-BRIDGE (*J. Annal. and Appl. Chem.*, **7**, 301—307).—The authors communicate the results of several experiments they have made to obtain nickel in a higher state of oxidation. The *modus operandi* was to precipitate nickel sulphate with sodium carbonate in presence of bromine at various temperatures. The degree of oxidation was ascertained by treating the products with potassium iodide and hydrochloric acid and titrating the liberated iodine.

From the experiments made, the authors conclude that the higher oxides of nickel are unstable compounds, and that an oxide higher than Ni_3O_5 can be obtained. They have not, however, succeeded in obtaining nickel dioxide, NiO_2.   L. DE K.

Purification of Thorium Oxide. By C. BÖTTINGER (*Zeit. anorg. Chem.*, **6**, 1).—Advantage is taken of the fact that a solution of thorium oxalate in warm ammonium oxalate is precipitated by strong hydrochloric acid; the ignited precipitate yields a pure oxide. A prescription for making cones for the Welsbach light is given.
                                                                A. G. B.

Sulphur Compounds of Thorium. By G. KRÜSS (*Zeit. anorg. Chem.*, **6**, 49—56; compare Abstr., 1893, ii, 574).—By heating thorium oxide in carbon bisulphide at a red heat, thorium oxysulphide, ThOS, coloured black with carbon, is obtained. The same compound is the product of heating ammonium thorium chloride, potassium thorium chloride, and thorium oxychloride respectively, in hydrogen sulphide. It has a light, brown colour.   A. G. B.

Complex Acids. Tungstovanadates and Ammonium Phosphomolybdates and Arsenomolybdates. By C. FRIEDHEIM (*Zeit. anorg. Chem.*, **6**, 11—26, 27—34; compare Abstr., 1893, ii, 282, 378, 472).—When a mixture of sodium paratungstate and sodium vanadate is fractionally crystallised, the salts $5Na_2O,6WO_3,3V_2O_5 + 38H_2O$ (Abstr., 1890, 14), $6(Na_2O,2WO_3),Na_2O,V_2O_5 + 29H_2O$, and $7(Na_2O,2WO_3)Na_2O,V_2O_5 + 66H_2O$ are obtained. The aqueous solution of the first of these salts, sodium ditungstosesquivanadate, is precipitated by barium chloride, silver nitrate, calcium chloride, and potassium chloride; the composition of the precipitate in each case is discussed (compare Rosenheim, Abstr., 1889, 762). When potassium salts are substituted for sodium salts in the method of preparation, no crystalline products are obtained. Ammonium salts yield ammonium paratungstotrivanadate, with evolution of ammonia.

The salts produced by the action of molybdic anhydride on ammonium arsenate and ammonium phosphate, and of ammonium

molybdate on ammonium arsenate and phosphate, have been analysed ; their formulæ are discussed. A. G. B.

Action of Heat on Ruthenium Alkali Nitrites. By A. JOLY and E. LEIDIÉ (*Compt. rend.*, **118**, 468—471) —The orange-red salt, very soluble in water, formed in neutral solution by adding the calculated quantity of potassium nitrite to a solution of ruthenium chloride has the composition $Ru_2(NO_2)_6,4KNO_2$, and the yellow salt, only slightly soluble in water, and formed in an alkaline solution, in presence of excess of alkali nitrite, has the composition, $Ru_2O(NO_2)_4,8KNO_2$; it crystallises with H_2O, but becomes anhydrous at 100° (compare Abstr., 1890, 17).

Ruthenium Sodium Nitrites.—When a solution of sodium nitrite is gradually added to a solution of ruthenium chloride at 60—80° until the liquid is neutral, an orange-red solution is obtained, which, on cooling, deposits the compound $Ru_2(NO_2)_6,4NaNO_2,4H_2O$ in orange-yellow, dichroïc, monoclinic prisms, very soluble in water, from which they can be repeatedly recrystallised without decomposing. When heated with dilute hydrochloric acid, the salt yields the nitrosochloride $Ru(NO)Cl_3,2NaCl$; when mixed with potassium hydroxide and saturated with chlorine, it gives off vapours of ruthenium peroxide. From 5 to 6 kilos. of this salt were obtained from 60 kilos. of iridium residues, rich in ruthenium, and hence sodium nitrite is of great service in the extraction of the metal from substances in which it is present in small quantity.

When the potassium salt $Ru_2O(NO_2)_4,8KNO_2$ is heated at 360° or 440° in a vacuum, there is sudden and almost explosive decomposition, nitrogen and nitrogen peroxide being evolved, and the residue, when treated with water, yields a solution of alkali nitrite quite free from ruthenium. The insoluble black residue has the composition $K_2O,3Ru_2O_5$, and its formation confirms the acidic character of perruthenic acid (Abstr., 1892, 282).

The sodium salt at 360° or 440° yields the compound Na_2O,Ru_4O_9, which cannot be a mere mixture of the alkali oxide and the ruthenium oxide, since the latter would decompose at 440°. At a dull red heat, the nitrite yields the oxide RuO_2, which retains only a trace of alkali after being washed with boiling water. If the temperature is so high that the alkali nitrite fuses, the greater part of the ruthenium is converted into the ruthenate K_2RuO_4. C. H. B.

Mineralogical Chemistry.

Hydrocalcite from Wolmsdorf. By B. KOSMANN (*Jahrb. f. Min.*, 1894, i, Ref. 260—261, from *Glückauf*, **28**, No. 38).—In the marble quarry at Wolmsdorf, near Landeck, a stalactitic cavern was recently laid bare, in which the roof was covered with a white consistent mass. This was found to be a hydrated calcium carbonate having the com-

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position represented by the formula $CaCO(OH)_4$. For this mineral, the author suggests the name of hydrocalcite.   B. H. B.

Taraspite from Vulpera, Switzerland. By C. v. JOHN (*Jahrb. f. Min.*, 1894, i, 257—258; from *Verhandl. k. k. geol. Reichsanst,* 1891, **3**).—The author has investigated taraspite from Vulpera, a mineral similar to the miemite of Zepče. It is derived from serpentine, and has the composition of a normal dolomite in which some of the magnesia is replaced by iron, and in which, as in the serpentine, some nickel is present. Taraspite therefore should be classed with miemite. Its composition is as follows :—

$CaCO_3$.	$MgCO_3$.	$FeCO_3$.	NiO.	Insol. in HCl.
54·78	42·83	2·02	0·14	0·82

B. H. B.

New Minerals from the Sjö Mine, Sweden. By L. J. IGEL-STRÖM (*Zeit. Kryst. Min.*, **22**, 467—472).—The author describes some additions to the numerous new antimony minerals found by him in the Sjö manganese Mine during the last 10 years.

1. *Lamprostibian* was found in June, 1893, and has been named from λαμπρός and *stibium*. It resembles highly laminated, specular iron ore, from which it is distinguished by its brighter colour. In thick pieces, it is opaque; but in thin layers, it is transparent with a blood-red colour. Its hardness is about 4. It is brittle and non-magnetic. Qualitative analysis shows it to be an anhydrous ferrous and manganous antimonate.

2. *Elfstorpite* is a hydrated, pale yellow, translucent, manganous arsenate, occurring in crystalline patches and in crystals probably of the rhombic system. Its name is derived from the Elfestorp Iron-works in the vicinity of the Sjö Mine.

3. *Chloroarsenian* occurs as minute, yellowish-green crystals of high lustre, apparently monosymmetrical or triclinic. It seems to consist of manganous arsenite.

4. *Rhodarsenian* is a red, transparent mineral occurring in globules in arseniopleite. Analysis gave results in accord with the formula $(10RO,As_2O_5) + 10(RO,H_2O)$, in which RO is MnO,CaO,MgO.

As an appendix to this paper, the author describes two new minerals from the same mine, descriptions of which he has already published in Swedish (*Geol. Fören. Förhandl.*, **14**, 307). These are *basiliite*, $(Mn_2O_3)_4,Sb_2O_5 + 7Mn_2O_3,3H_2O$, and *sjögrufvite*,

$$2[R_3(AsO_4)_2],R_2(AsO_4)_2,6H_2O.$$ B. H. B.
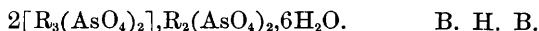
Powellite from a new Locality. By G. A. KÖNIG and L. L. HUBBARD (*Zeit. Kryst. Min.*, **22**, 463—466).—The material examined was found in the autumn of 1892 in the 14th level of shaft No. 8 of the South Hecla Mine, Michigan. It has a hardness of 4·5, a sp. gr. of 4·349, a pale, bluish-green colour, and a vitreous lustre. Analysis gave the following results.

	MoO₃.	WO₃.	CaO.	MgO.	Fe₂O₃.	SiO₂.	Cu.
I.	65·74	4·50	27 41	—	—	—	—
II.	67·84	1·65	27·30	0·16	0·96	1·52	trace

B. H. B.

Chemical Composition of Chondrodite, Humite, and Clinohumite. By S. L. PENFIELD and W. T. H. HOWE (*Amer. J. Sci.*, [3], **47**, 188—206).—The authors show that the minerals of the humite group are not identical in composition, and that they can be expressed by the following formulæ.

Chondrodite .... $Mg_3[Mg(F\cdot OH)]_2[SiO_4]_2$.
Humite .... $Mg_5[Mg(F\cdot OH)]_2[SiO_4]_3$.
Clinohumite .... $Mg_7[Mg(F\cdot OH)]_2[SiO_4]_4$.

The variation in composition is intimately connected with the crystallisation, the three minerals forming a crystallographic series in which the vertical axes increase from chondrodite to clinohumite. By dividing the vertical axes by 5, 7, and 9 respectively, the quotients become practically identical, and it is an interesting fact that the divisors correspond with the number of magnesium atoms in the formulæ deduced. B. H. B.

Axinite from Bourg d'Oisans, Dauphiné. By P. JANNASCH and J. LOCKE (*Zeit. anorg. Chem.*, **6**, 57—71).—In continuation of a series of tourmaline analyses (Abstr., 1889, 472), the authors have made two careful analyses of axinite from Dauphiné with a view to affording information regarding the constitution of silicate-borates. The mean results of the two analyses were as follows.

SiO₂.	B₂O₃.	Al₂O₃.	Fe₂O₃.	FeO.	MnO.	CaO.	MgO.
42·88	6·02	18·24	0·62	7·10	1·06	19·89	2·23

		K₂O.	Na₂O.	H₂O.	Total.		
		0·11	0·36	2·14	100·65		

These results are in accord with the empirical formula

$$Si_6O_{23}R'''_4R''_4R_2,$$
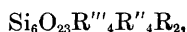
or $Si_6O_{23}(Al,B)_4(Ca,Fe,Mn,Mg)_4H_2$ (compare this vol., ii, 55).
B. H. B.

Moldavite from Radomilic, in Bohemia. By C. v. JOHN (*Jahrb. f. Min.*, 1894, i, Ref., 266—267; from *Jahrb. k. k. Geol. Reichsanst*, **39**, 473—476).—The author has analysed the moldavite or bottlestone from Radomilic (described by Woldrich in 1888) with the following results.

	SiO₂.	Al₂O₃.	Fe₂O₃.	FeO.	CaO.	MgO.	K₂O.	Na₂O.	Ignition.
I.	82·28	10·08	—	2·03	2·24	0·98	2·20	0·28	0·06
II.	77·75	12·90	—	2·60	3·05	0·22	2·58	0·26	0·10
III.	77·69	12·78	2·05	1·45	1·26	1·15	2·78	0·78	—

I, light green variety; II, dark green; III, light brown. The high percentage of potash is noteworthy. Although the nature of

the occurrence appears to indicate a natural origin, the author is unable to decide whether the mineral is a natural or an artificial product.   B. H. B.

Minerals from York Haven, York Co., Pa. By C. H. EHRENFELD (*J. Anal. Appl. Chem.*, **7**, 4—5).—An analysis of weathered *stilbite* gave the following results.

SiO₂.	Al₂O₃.	CaO.	K₂O.	H₂O.
52·07	22·11	12·17	trace	13·57

The mineral occurs on the exposed surfaces of the rock as a white mass, without the least sign of crystallisation. Hardness 2. It is readily gelatinised by hydrochloric acid.

An analysis of *chabasite* gave the following results.

SiO₂.	Al₂O₃.	CaO.	K₂O.	H₂O.
50·69	19·46	7·28	1·38	21·32

The mineral occurs in small, almost cubical rhombohedra, 0·5 mm. to 2 mm. square, and translucent. Specific gravity, 2·18. It is not gelatinised by hydrochloric acid.

An analysis of *augite* showed—

SiO₂.	Al₂O₃.	FeO.	CaO.	MgO.	H₂O.
51·27	10·01	9·11	13·23	13·60	1·64

It occurs near to or mixed with stilbite, and has a dark bronze-green colour, shining lustre, and crystalline structure. Specific gravity, 3·008.

Sphalerite occurs as a thin coating between layers of blue limestone, but the author could not get it in a sufficiently pure condition for the purpose of analysis.   L. DE K.

Topazolite and Melanite. By M. PINERS (*Zeit. Kryst. Min.*, **22**, 479—496).—The determination of minerals of the garnet group presents many difficulties. Under the head of lime-iron garnet, for example, there are classed two entirely different members of the group, topazolite and melanite. In order to definitely determine the composition of these two members, the author has made careful analyses of topazolite from the Mussa Alp, in Piedmont; from Wurlitz, in the Fichtelgebirge; and from a new locality in the Southern Tyrol; as well as of melanite from the Burgumer Alp, in Pfitsch; from the Margola, in the Southern Tyrol; and from a new locality near Zermatt. The results show that topazolite is essentially a pure lime-iron garnet, free from titanic anhydride, occurring, unless darkened by a foreign pigment, as pale yellow or greenish-yellow crystals. Melanite, on the other hand, is the name that should be given to titaniferous lime-iron garnets, as indicating the fact that they are invariably black.   B. H. B.

Serpentine from Brewster, New York. By G. FRIEDEL (*Zeit. Kryst. Min.*, **22**, 580—581; from *Bull. Soc. Fran. Min.* **14**, 120).—Among the numerous pseudomorphous forms in which serpentine

occurs at the Tilly Foster iron mine, near Brewster, New York, there are compact masses that have a perfect cubical cleavage, and also in places an octahedral cleavage, the cleavage-planes exhibiting a pearly lustre. The author, however, comes to the conclusion that the phenomenon is not one of cleavage, but that the entire mass consists of a network of rhombic lamellæ having the chemical composition of serpentine, which cross at the angles of the octahedron and cube, and whose interstitial space is filled with a dense substance of the same composition. B. H. B.

Meteorites of Knyahinya and Hainholz. By E. PRIWOZNIK (*Jahrb. f. Min.*, 1894, i, Ref., 274—275; *Öesterr. Zeit. Berg. Hütt.*, 1892, No. 39).—The stone meteorite that fell on June 9, 1866, at Knyahinya, in Hungary, contained 5·03 per cent. of magnetic constituents, and 94·97 non-magnetic. The latter was pulverised, and treated with hydrochloric and nitric acids, with the result that 47·56 per cent. passed into solution (Analysis I), whilst 52·774 remained insoluble (Analysis II). The analytical results were as follows.

	SiO_2.	CaO.	MgO.	Fe.	Ni.	FeO.	Al_2O_3.	Cr_2O_3.	Na_2O.	S.
I.	8·8	2·9	18·3	2·4	0·32	11·60	1·14	—	—	2·10
II.	33·4	3·0	9·1	—	—	4·6	1·8	0·004	0·87	—

The metallic grains isolated by means of the magnet from the decomposed aerolite of Hainholz, near Paderborn, gave on analysis

Fe.	Ni.	Co.	P.	C.	Total.
92·4	7·0	0·2	0·298	—	99·898

B. H. B.

Physiological Chemistry.

New Animal Calorimeter. By J. S. HALDANE, W. H. WHITE, and J. W. WASHBOURN (*J. Physiol.*, **16**, 123—139).—The calorimeter described embodies the principle of D'Arsonval's. The test experiments described, including some in which animals were used, show it to be accurate, and its accuracy can at any time be easily tested. Moreover, it can be used simultaneously as an accurate respiration apparatus. For a full description of the instrument, reference must be made to the original paper, where an illustration exhibits the principal points in its construction. The action of the calorimeter is as follows. In one copper chamber the animal is placed; in the other hydrogen is burnt, both chambers being shut. The heat given off from the animal warms its chamber, and thus increases the pressure of the air in the space between the two upper walls of its chamber. This would lead to movement of the fluid (oil of erigeron) in a manometer, one limb of which communicates with the air space of the one chamber, the other with that of the other chamber. In the other chamber, hydrogen is kept burning, and the pressure of the

air in its surrounding space is thus increased, and tends to move the fluid in the manometer in the opposite direction. If the fluid in the manometer remains stationary, the amount of heat given off by the animal is equal to that produced by the burning hydrogen; and during an experiment the manometer is kept stationary by turning up or down the hydrogen flame. The amount of hydrogen burnt is estimated, and knowing the heat of combustion of hydrogen, it is possible to calculate the heat produced by its combustion in the experiment, which is equal to that given off by the animal.

For testing purposes, each chamber is furnished with a jet of hydrogen. W. D. H.

Influence of Time on the Absorption of Carbonic Oxide by Blood. By N. GRÉHANT (*Compt. rend.*, 118, 594—595).—When a dog is made to breathe artificially a mixture of air and carbonic oxide containing 100 c.c. of the latter in 100 litres, after half an hour the blood contains 6·0 c.c. of carbonic oxide in 100 c.c.; after an hour, 9·2 c.c.; after two hours, 10·0 c.c.; and after two hours and a half 9·3 c.c. With the proportion of carbonic oxide specified, the volume absorbed by the blood becomes practically constant after an hour.

With a mixture containing only 10 c.c. of carbonic oxide in 100 litres, the law of absorption is different and the proportion of carbonic oxide in the blood gradually increases. After half an hour, 100 c.c. contain 1·42 c.c. of the gas; after an hour, 2·05 c.c.; after an hour and a half, 2·9 c.c.; after two hours, 3·15 c.c.; after two hours and a half, 3·6 c.c. C. H. B.

Behaviour of the Phosphorus in the Digestion of Caseïn. By E. SALKOWSKI (*Exper. Stat. Record*, 5, 428; from *Centr. Med. Wiss.*, 1893, 385—386).—It is frequently stated that in the pepsin digestion of caseïn the phosphorus is not dissolved, but is separated as insoluble paranuclein. The author finds that much of the phosphorus is dissolved by the digestive fluid, and that only about 15 per cent. is contained in the paranuclein. It may therefore be assumed that the phosphorus has a definite function. N. H. M.

Absorption of Iron. By A. B. MACALLUM (*J. Physiol.*, 16, 268—297).—The experiments consisted in administering iron compounds to animals, and by microchemical methods determining whether the absorbing cells of the alimentary tract take up any. Inorganic compounds were found to be absorbed. If the dose is small, absorption occurs only in a small part of the duodenum adjacent to the pylorus. With larger doses the area increases. With small doses, the iron of the unabsorbed salt is precipitated by bile and other secretions as hydroxide, which is not assimilable; large doses first destroy the alkalinity of these liquids, so that the excess of salt remains in solution and undergoes absorption.

The intestinal epithelium cells transfer the absorbed iron at once to the underlying elements, but if the dose is large the epithelial cells will still be found containing some. Although some of the sub-

epithelial leucocytes appear to carry it into the general circulation, probably the more important agent in the transference is the blood-plasma.

Marfori's albuminate and the commercial " peptonate " of iron, when administered to guinea pigs, stimulate the leucocytes to invade the epithelial layer of the villi.

Of the organic iron compounds belonging to the chromatin or nucleïn class, that present in egg-yolk (Bunge's hæmatogen) undergoes absorption. For several days after feeding, the cytoplasm of the liver cells yields marked evidence of an iron-containing chromatin. The mode of absorption of the yolk chromatin is obscure, and appears to be connected with the absorption of the fat with which the iron compound is closely associated in yolk.　　　　　　W. D. H.

Influence of Ichthyol on Metabolism. By O. HELMERS (*Virchow's Archiv*, **135**, 135—146).—Ichthyol influences the metabolism of proteïd in the human body only in a slight degree. Its action, such as it is, is to diminish the decomposition and favour the assimilation.

About a third of the sulphur in the drug circulates in the body juices, and is excreted finally in the urine. That which passes from the body by the fæces has also in part circulated in the body, and is excreted by the intestinal glands.　　　　　　W. D. H.

Dietetic Value of different Kinds of Bread. By G. MENICANTI and W. PRAUSNITZ (*Zeit. Biol.*, **30**, 328—367).—Bread made with yeast leads to smaller formation of fæces than bread made with the same flour with leaven; wheat bread is also better in this direction than rye bread, whilst bread made with a mixture of wheat and rye flour is intermediate. Bread made from the decorticated grain also leads to a less abundant excrement. This excrement appears to be for the most part due to the residues of intestinal juice, and not so much to unabsorbed food. The harder the bread, and the coarser the flour, the greater is the amount of intestinal juice secreted. The finer German meals used contain particles averaging 0·1 to 0·14 mm. in diameter, but reference to other writers shows that the size varies considerably in different parts of the country.　　　　　　W. D. H.

Influence of Sugar and of Smoking on Muscular Work. By V. HARLEY (*J. Physiol*, **16**, 97—122; and *Proc. Roy. Soc.*, **54**, 480). —The experiments were performed with Mosso's ergograph, and show that the periods of digestion, as well as the kinds of food, have a marked influence on voluntary muscular energy; but, irrespective of this, there is a periodical diurnal rise and fall in the power of doing work, the *minimum* being about 9 A.M., the maximum about 3 P.M. Regular muscular exercise increases the size and power of the muscles, and delays the onset of fatigue. The amount of work performed on sugar alone is almost equal to that obtained on a full diet, but fatigue comes on sooner. Sugar acts as a source of muscular energy when taken alone, or in addition to other articles of diet. Moderate smoking may have a slight influence in diminishing the

power of doing muscular work, but it stops neither the morning rise nor the evening fall. W. D. H.

Asparagine in the Organism. By J. LEWINSKY (*Chem. Centr.*, 1894, i, 53—54; from *Centr. Med. Wiss.*, 1893, 709—718).—In the quantitative estimation of amido-acids, such as asparagine, by Schultze's method, in which half the contained nitrogen is eliminated as ammonia, and the other half as aspartic acid, concentrated hydrochloric or sulphuric acid has hitherto been used ; the present research, however, shows that it is better to employ 20 per cent. acid.

After removing the proteïd matter from blood or organs, asparagine or aspartic acid can be precipitated by copper acetate; the copper precipitate contains 60 to 80 per cent. of the amido-acid. From the copper precipitate, the percentage of asparagine can be reckoned from the amounts of copper and nitrogen. The estimation of asparagine is not possible by this method in organs, on account of the varying amount of extractive nitrogen they contain.

After feeding a dog on asparagine (4 to 6 grams per kilo. of body weight), asparagine could not be found in the liver, spleen, or carotid blood. The blood, however, shows an increase of extractive nitrogen up to the fifth hour after the dose, when the absorption maximum appears to occur. In six hours, two-thirds of the asparagine given is excreted as urea. W. D. H.

Proteïds of Spleen and Thyroïd. By F. GOURLAY (*J. Physiol.*, 16, 23—33).—A full account of experiments, already published in a preliminary communication (Abstr., 1893, ii, 425). W. D. H.

Effect of Calcium Phosphate in Food on the Ash of Milk. By J. NEUMANN (*Exper. Stat. Record*, 5, 639—640; from *Milch Zeit.*, 22, 701—704).—Three cows had each 100 grams of calcium phosphate added to their usual food—brewer's grains (22·5 kilos.), hay (4 kilos.), oat straw (2 kilos.), and salt (20 grams). The experiment lasted about 5 weeks. The average percentage amount of lime and phosphoric acid in the milk, before and after adding the phosphate to the food, was as follows :—

	CaO.	P_2O_5.
Without calcium phosphate	0·1479	0·1960
With ,, ,,	0·1592	0·2132

An experiment which lasted less than two weeks gave no definite results.

The results indicate a slight increase in both constituents, both percentage and absolute, when calcium phosphate is given with a food already containing sufficient amounts of ash constituents. The increase is only apparent after three or four weeks, which perhaps accounts for the negative results obtained by others. The production of so-called "phosphate-milk" with a high percentage of phosphate is considered impossible (compare Abstr., 1893, ii, 582).

N. H. M.

Combinations of Chlorine in Urine. By A. BERLIOZ and E. LÉPINOIS (*J. Pharm.*, **29**, 288—296).—In addition to mineral chlorides, the urine contains organic compounds containing chlorine. This fact is of importance in determining the variations in the amount of chlorine in healthy and pathological urines; and still more valuable would be the result if it were possible to simultaneously examine the chlorine compounds in the gastric juice.   W. D. H.

Odour of Benzoic acid. By J. PASSY (*Compt. rend.*, **118**, 481—482).—Benzoic acid, prepared by various methods, has no odour while in the crystalline condition, but if volatilised in the vapour of water, or dissolved in dilute alcohol, or if a solution in a 0·6 per cent. aqueous solution of sodium chloride is inhaled in the form of spray, the characteristic odour is at once perceived. These results, together with the observations previously made on coumarin, vanillin, &c., indicate that apparently inodorous substances may be divided into two groups, namely, those that are truly inodorous under various conditions, and those that are only inodorous under certain particular conditions, but distinctly odorous under other conditions.

                                                        C. H. B.

Action of Salts on Tubifex Rivulorum. By S. RINGER and H. SAINSBURY (*J. Physiol.*, **16**, 1—9).—In a former series of papers, the authors have shown the importance of calcium salts in vital and coagulation processes, and the antagonism existing between calcium and potassium. The present experiments on the fresh-water worm *Tubifex rivulorum* confirm and extend these observations. In tap water, the worms live an indefinite time; in distilled water they are dead and disintegrated within 24 hours. That it is the minute quantities of calcium salts in the river water which prevents this disintegration is shown by adding a calcium salt, in small quantities, to distilled water; in this the worms live a long time. The quantity of calcium salt may, however, be increased enormously without any untoward result, it being very indifferent to the tissues. Calcium salts, both in minimal and massive doses, antagonise the paralysing influence of potassium salts; and whilst a minimal dose of calcium salt has extraordinary powers of inhibiting the action of large quantities of potassium salts, a massive dose of the latter is most easily overcome by a massive dose of a calcium salt.

Sodium contrasts with potassium in the relative feebleness of its action, maintaining its character as an indifferent element.

                                                        W. D. H.

Effect of Hydrogen Cyanide on different Insects. By R. SCHMIDT (*Exper. Stat. Record*, **5**, 593—594; from *Calif. Stat. Rep.*, 1891-92, 233—237).—A number of insects (24 species) were exposed to the action of hydrogen cyanide; it was found that some of the *Coleoptera* were alive after 68 minutes. The effect of the gas and the time of exposure is given in tables.   N. H. M.

Chemistry of Vegetable Physiology and Agriculture.

Effect of Potassium Salts on Nitrification. By J. DUMONT and J. CROCHETELLE (*Compt. rend.*, **118**, 604—606; compare this vol., ii, 116).—In the first experiments, now described, moor soil (containing humus 18·5, lime 0·285, per cent.) was treated with varying amounts of potassium carbonate and sulphate respectively, and kept for 20 days at about 25°. Where no potassium salt was added, the amount of nitric nitrogen formed was 24—25 per million; with carbonate, applied in quantities of 0·1 to 6 per cent., the nitric nitrogen increased to 47 (with 0·1 per cent.), to 65 (with 0·5 per cent.), and to 438 with 4·5 per cent., after which it dimished (to 407 and 375) with 5 and 6 per cent. respectively. The results with potassium sulphate were very irregular, the nitric nitrogen being raised to 50 per million of soil with 0·5 per cent. of sulphate, whilst with the larger quantities (up to 5 per cent.) the amounts varied between 18 and 27 per million.

When, however, calcium carbonate (2·5 per cent.) was given to the soil, in addition to the potassium sulphate, there was a regular and marked increase in the amount of nitric nitrogen produced; for example, with no calcium carbonate or potassium sulphate, 26 parts of nitric nitrogen was produced; with carbonate alone, 30 parts; with carbonate and 0·5 per cent. of sulphate, 75·6 parts; with carbonate and 5 per cent. of sulphate, 189 parts per million. Potassium sulphate is, therefore, rendered efficacious by the presence of calcium carbonate, with which it undergoes decomposition, yielding potassium carbonate. The change is very rapid. Thus, a solution of potassium sulphate filtered through moor-soil is almost colourless, but when calcium carbonate is added the solution becomes coloured, especially when the amount of potassium sulphate is increased.

The results are of practical importance in horticulture when soils rich in humus are employed. N. H. M.

Production of Ammonia in the Soil by Microbes. By E. MARCHAL (*Bull. Acad. roy. Belg.*, [3], **25**, 727—771).—Two lots of soil (250 grams), to which a 10 per cent. of albumin solution (2·5 c.c., containing 0·001 per cent. of ferrous sulphate to prevent coagulation) had been added, were sterilised. The one was kept sterilised, whilst the other was inoculated with a few c.c. of soil extract. After 20 days, the sterilised soil, like the soil at the commencement, contained only traces of ammonia; the inoculated soil contained 34·2 milligrams of ammonia. This confirms the results obtained by Müntz and Coudon (Abstr., 1893, ii, 291), showing that ammonia is produced in soil by microbes and not by a chemical process.

A number of moulds, yeasts, and bacteria were isolated from soils of different kinds, and their action in dilute albumin solutions determined.

As regards bacteria, *Bacillus arborescens, B. coli communis* var., *B. figurans, B. fluorescens putidus,* and *liquefaciens, B. mesentericus vulgatus, B. mycoïdes, B. subtilis, B. termo, B. janthinus, Micrococcus albicans, Proteus vulgaris,* and *Sarcina lutea,* all produced much ammonia. Most of the other bacteria produced some ammonia; but a few (a non-liquefying *Proteus* and a long, liquefying bacillus) gave no ammonia. The organisms which produced no ammonia developed only slightly. Ammonisation thus differs from nitrification in being brought about by a very large number of microbes.

In many cases, the amount of ammonia formed was determined; it was found that *B. mycoïdes* was much the most active of the soil organisms.

About 30 moulds were isolated, and their action on albumin investigated, with the result that nearly all were found to produce ammonia. The most active was *Cephalothecium roseum,* which produced 25 milligrams in 50 c.c. in two weeks. It is supposed that in arable soil, where moulds are present only in small amounts, the action of bacteria must predominate, whilst in humus, and soils rich in organic matter, there is no doubt that the moulds take an active part in the mineralisation of organic nitrogen.

The *Bacillus mycoïdes* (first described by Flügge as " Erde Bacillus "), being evidently the most important, was further investigated. It occurs constantly in surface soils, and is present in the air and in natural waters. In decomposing albumin, it produces a strongly alkaline solution, due to ammonium carbonate; the carbon is mainly converted into carbonic anhydride, but formic, propionic, and butyric acids are formed in small quantities; the sulphur is oxidised to sulphuric acid. No hydrogen or nitrogen are eliminated in the free state. Slight alkalinity is favourable to the development of the bacillus, but it will develop in solutions containing $0·05$ per cent. of sulphuric acid, although not in presence of $0·1$ per cent. It will also develop in $0·2$ per cent. solutions of potash. A temperature of $30°$ is the most suitable; below $5°$ only traces of ammonia are produced, and at $42°$ none at all. The bacillus will not develop in an atmosphere of hydrogen or carbonic anhydride except in solutions of organic matter and nitrate. Under these conditions, it develops well, the necessary oxygen being obtained from the nitrate, which becomes reduced to nitrite and ammonia. As regards the action in nitrogenous matter other than egg-albumen, the bacillus decomposes other proteïds, also leucine, tyrosine, creatine, and asparagine, but not urea; it also fails to develop in solutions of ammonium salts and nitrates, except under the conditions already described. When *B. mycoïdes* is grown in solutions of albumin and carbohydrates, the solution becomes turbid, shows an acid reaction, and the albumin is precipitated. Acid is formed when glucose, saccharose, lactose, dextrose, and starch are employed, slightly with inuline, but not with gums. The reaction is not definite; under the influence of a zymose secreted by the microbe, the albumin redissolves, and the solution eventually becomes alkaline.

It is concluded that " nitratation " of soil nitrogen is preceded by " ammonisation," followed by " nitrosation," and that the ammonia

producing bacillus can act both as an oxidising and as a reducing agent according to the conditions.   N. H. M.

Vegetable Cell Membranes. By E. SCHULZE (*Zeit. physiol. Chem.*, **19**, 38—69; compare Abstr., 1890, 283; 1892, 907).—The cell membranes, prepared from various seeds by removal of fat and proteïd matter by dilute sodium hydroxide, were in confirmation of previous researches found to consist very largely of hemi-celluloses. These, by treatment with dilute mineral acids, yield a pentose (arabinose, or xylose in different cases), and often galactose in addition. The seeds of the blue lupin were those to which special attention was directed ; the yield of galactose here is very great. Pentosan, galactan, and mannan appear to be very widely distributed, and act as the mother substances of the respective carbohydrates.

Quantitative analysis gave the following results.

Proteids (N × 6·25) ....   7·25
Organic material free from N........   89·85
Ash..............................   2·90
                                    ———
                                    100·00

Another analytical point made out is the very low percentage of cellulose ; in the case of the blue lupin, it is only 3·9 per cent.

E. Gilson (*La Cellule*, **9**, 397—440), in a recent investigation of cell membranes in plants, doubts the existence of mannoso-cellulose, and describes a substance he calls paramannan, which, mixed with cellulose, constitutes mannoso-cellulose. The author's previous views on the subject are here upheld. Gilson's paramannan is probably not identical with mannoso-cellulose, but is a hydrate of it.

The paper concludes with a classification of the constituents of cell walls. The author recommends that the term *cellulose* should be restricted to dextroso-cellulose, that is, to cellulose which yields dextrose, and the other celluloses should be called *hemi-celluloses*. In addition to these, *amyloïd* and *mucus-yielding* substances are present. Reiss has designated mannose (seminose) *reserve cellulose*, that is, it is dissolved and used in the growth of the seedling ; this term, however, must be extended to include part at least of the hemi-celluloses.
                                                    W. D. H.

The Taking Up of Calcium Chloride by Plants. By E. JENSCH (*Zeit. angw. Chem.*, 1894, 111—112).—Raspberries and strawberries growing round the edges of puddles below the Schwarzberger smelting works, in the Erzgebirge, were noticed to be generally of an unusually large size. The plants growing on the drier places generally had badly shaped fruit covered with a white substance, whilst the fruit of the plants nearer the water was very large and brightly coloured. All the fruit differed from that of more distant plants in being more quickly perishable. The fruit and stems, especially of the raspberries, tasted strongly of calcium chloride ; the leaves only slightly. The origin of the calcium chloride was an accident which had taken place six months previously, when a quantity of a solution of calcium and copper chlorides flowed out of

an extracting drum over the ground. The following analyses are given.

	Dry matter.	Ash.	Cl.
Healthy raspberries..............	17·41	0 88	—
Diseased ,, from dry ground	11·52	1·96	0·20
., ,, ,, damp ,,	8·35	1·52	0·13
Strawberries, healthy	12·03	0·72	—
,, diseased	7·16	1·24	0·04

All the ashes contained traces of copper.   N. H. M.

Analytical Chemistry.

Modified Litre Flask. By W. B. GILES (*Chem. News*, **69**, 99—100).—In the neck of the flask above the litre mark, the author provides an enlargement, and a second mark indicates an additional volume of 100 c.c. When preparing a solution, 1100 c.c. is allowed for, and the solution made rather too strong, the 100 c.c. in excess serving for the necessary standardising tests, and, as exactly a litre remains, the final adjustments to the desired strength are much facilitated.   D. A. L.

Use of Sodium Hydrogen Tartrate in Alkalimetry. By A. BORNTRAEGER (*Zeit. angw. Chem.*, 1894, 54—55).—The author, in reply to several critics, states as his opinion that sodium hydrogen tartrate when *pure* is the most suitable substance for standardising normal alkalis.   L. DE K.

Detection of Free Mineral Acids in presence of Organic Acids. By E. NICKEL (*Chem. Zeit.*, **17**, 1670).—The author recommends the following process for the detection of, say, hydrochloric acid in vinegar :—The sample is mixed with a large quantity of phloroglucinol, and then boiled for a while with a piece of pine wood or bamboo. After further contact for about 12 hours, the wood will assume the well-known characteristic colour if any free mineral acid be present.   L. DE K.

Estimation of Iodine in Presence of Bromine and Chlorine. By M. GRÖGER (*Zeit. angw. Chem.*, 1894, 52—54).—The process is based on the fact that alkali iodides are converted into iodates by the action of potassium permanganate, whilst bromides or chlorides are not affected.

The solution, which should contain no ammonia, is heated on a boiling water bath, and a 4 per cent. solution of potassium permanganate is added until the supernatant liquid turns decidedly red. The excess of permanganate is then reduced by adding a few drops of alcohol. The liquid is filtered and the precipitate thoroughly washed

by decantation. The author recommends working on a small quantity of the iodide mixture, so as to have only about 0·05 gram of iodine present; otherwise there is too much precipitate, and the washing takes a very long time. The filtrate, after cooling, is mixed with 0·5 gram of potassium iodide, acidified with hydrochloric acid, and the liberated iodine is then titrated with sodium thiosulphate. One-sixth part of the iodine found was originally present in the sample. To estimate iodine in the crude article, 0·5—1 gram is dissolved in its own weight of sodium hydroxide contained in a little water. The solution is made up to 250 c.c., and 25 c.c. is pipetted off and treated with permanganate as directed. The test-analyses are very satisfactory.   L. DE K.

Detection of Iodates in Alkali Iodides. By M. SPICA (*Gazzetta,* **24**, i, 91—95 ; compare Robineau and Rollin, Abstr., 1893, ii, 183). —Small quantities of iodate in potassium iodide, employed for medicinal purposes, may be detected by taking advantage of the fact that barium iodate requires 1736 parts of water at 15° for its solution. Any precipitate deposited on adding barium chloride to a solution of potassium iodide may be due to the presence of a carbonate, iodate, or sulphate. If the precipitate consists of barium iodate, it should be soluble in hot concentrated hydrochloric acid, and should again separate on diluting with water. 0·002 gram of potassium iodate in 100 grams of potassium iodide can be detected by this test.
                                                    W. J. P.

Estimation of Ammonia in Presence of Sulphides or Cyanides. By E. HENRY (*Bull. Soc. Chim.*, [3], **9**, 1018).—In the usual method of distillation with alkali, appreciable quantities of hydrogen sulphide or cyanide are liable to pass over when sulphides or cyanides are present. These should, therefore, be precipitated with basic lead acetate before distilling.   JN. W.

Estimation of Nitric acid with the Nitrometer. By E. HENRY (*Bull. Soc. Chim.*, [3], **11**, 24—27).—In the ordinary forms of nitro-

meter suitable for the analysis of solids, the funnel is usually ground into the main tube, and is liable, therefore, on the one hand, to be blown out by the evolved gas, or, on the other hand, to be crushed by the fingers of the operator. This defect is remedied in the instrument depicted. The funnel forms an extension of the reaction tube, and the solid is dissolved in it, instead of in the latter. The upper end, for this purpose, is stoppered, and the tap at the lower end provided with a channel of unusually large diameter. When the substance is completely dissolved, the solution is washed into the mercury tube with sulphuric acid in the usual way. The reaction is best carried out at a low pressure to diminish the error due to dissolution of nitric oxide in the acid. JN. W.
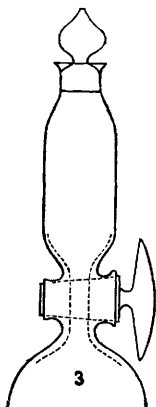
Detection of Nitrites in Urine. By A. JOLLES (*Zeit. anal. Chem.*, **32**, 762—766).—In consequence of the absorption of iodine by both the normal and pathological constituents of urine, the usual test for nitrites with potassium iodine and starch paste is not sufficiently sensitive, especially in view of the poisonous effect of the introduction of mere traces of nitrites into the blood. The lower limit of the test is not constant, but in a specimen of albuminous urine experimented with, no smaller quantity than 0·003 gram of N_2O_3 in 10 c.c. could be detected. The reaction with sulphanilic acid and α-naphthylamine will detect 0·000032 gram of N_2O_3 in 100 c.c. The urine must be decolorised by warming to 40° and shaking with a pinch of blood charcoal. 100 c.c. is then placed in a cylinder with a good ground stopper, acidified with sulphuric acid, then treated with 1 c.c. of sulphanilic acid, and, after a few minutes, with 1 c.c. of α-naphthylamine, and the cylinder stoppered air-tight. With the above quantity of nitrite, the rose-red colour requires 25 minutes for development.

Schäffer's reaction (see Deventer, Abstr., 1893, ii, 298) is almost equally sensitive, and can be applied to as little as 3 c.c. of the decolorised urine. This quantity is mixed in a test tube with an equal volume of acetic acid (1 : 10) and then 2, or at most 3, drops of potassium ferrocyanide (1 : 20). In presence of a nitrite, a yellow colour results from the oxidation of the ferrocyanide to ferricyanide. For highly dilute solutions of nitrites, the author is unable to confirm Deventer's quantitative results, and can suggest no better means for quantitative estimation than Trommsdorf's zinc iodide-starch method), applied to the decolorised urine, and executed as rapidly as possible. The most suitable quantity of the Trommsdorf solution to be used must be ascertained in each case as it is not constant. M. J. S.

Rapid Method for the Estimation of Phosphorus in Titaniferous Iron Ores. By C. BASKERVILLE (*J. Anal. and Appl. Chem.*, **7**, 194—196).—2 grams of dried and finely-powdered ore is thoroughly mixed with 20 grams of a mixture of 10 parts of sodium carbonate and 1 part of potassium nitrate and fused in a spacious platinum crucible. After cooling, the mass is repeatedly boiled with water, and the liquid, measuring about 300 c.c., is filtered, the insoluble

matter being well washed with hot water ; 25 c.c. of solution of ferric chloride, containing about 0·1 gram of iron is added ; the solution is acidified with hydrochloric acid, boiled, and precipitated with ammonia. After collecting and washing, the iron precipitate is dissolved in 40 c.c. of hot nitric acid (sp. gr. 1·43), 25 c.c. of strong ammonia is added, the liquid heated or cooled to 85°, and mixed with 30 c.c. of molybdate solution. After well shaking for five minutes, the molybdate precipitate is collected, and finally titrated according to the Manby-Handy method. L. DE K.

Estimation of Phosphoric acid by titrating the Molybdic Precipitate. By H. PEMBERTON (*Chem. Centr.*, 1894, **1**, 105 ; from *J. Amer. Chem. Soc.*, **15**, 382—395).—1 gram of the phosphate is dissolved in nitric acid and diluted with water to 250 c.c.; 25 c.c. is neutralised with ammonia, and then mixed with 5 c.c. of nitric acid (sp. gr. 1·4) ; 10 c.c. of a saturated solution of ammonium nitrate and 20 c.c. of water is next added, and the whole heated to boiling. An aqueous solution of ammonium molybdate (90 grams per litre) is now added in portions of 5 c.c. as long as a precipitate is produced. This is washed by decantation, a filter being also used, and then dissolved in a known volume of standard alkali. After adding phenolphthaleïn, the excess of alkali is titrated back with standard acid.

If 1 c.c. of the alkali is to correspond with 0·001 gram of phosphoric anhydride, its strength should be 0·3265—normal.

L. DE K.

Decomposing Silicates by Concentrated Hydrochloric acid under Pressure. By P. JANNASCH (*Zeit. anorg. Chem.*, **6**, 72).— The author claims priority for this method, which is effected in a platinum cylinder contained in a glass tube, the pressure on which is equalised by enclosing it in a Mannesmann tube containing ether.

A. G. B.

Solvent Action of Tartrates on Metallic Hydroxides. By H. N. WARREN (*Chem. News*, **69**, 125).—The author points out that the solvent action of normal tartrates is not restricted to the hydroxides and carbonates of ferric, cupric, and antimoniacal origin, but extends also to the ferrous, zinc, manganese, nickel, cobalt, chromium, aluminium, barium, strontium, magnesium, calcium, bismuth, and tin precipitates. As regards the last two metals. this point appears to be frequently overlooked by analysts ; cadmium carbonate is practically insoluble in this medium, and may therefore be separated from the copper compound by digesting such a mixture with a normal tartrate.

D. A. L.

Electrolytic Separations. By E. F. SMITH (*Zeit. anorg. Chem.*, **6**, 40—42 and 43—44).—It is pointed out that Freudenberg's observations on this subject (Abstr., 1893, ii, 506) are not new, but in most cases confirm the work of Smith and his collaborators.

The second paper is a continuation of a discussion with Classen.

A. G. B.

Electrolytic estimation of Copper in Invert-Sugar Determinations. By B. B. ROSS (*J. Anal. and Appl. Chem.*, **7**, 83—86).— The author has modified Formanek's process and operates as follows.

The precipitation of the cuprous oxide is effected in a beaker, and the precipitate is at once brought upon an asbestos filter in an ordinary funnel, and washed with hot water. The precipitate need not be completely transferred to the filter, which is replaced in the beaker, and the funnel is then rinsed with weak nitric acid containing 4 c.c. of acid (sp. gr. 1 42) to 100 c.c. of solution. The acid is added to the contents of the beaker until there is about 200 c.c. of liquid, and, after the platinum electrodes are introduced, connection is made with a battery giving a current equivalent to 0·5—0·7 c.c. of electrolytic gas per minute. The anode employed is a flat spiral of platinum wire of Luckow's pattern, and rests on the bottom of the beaker, whilst a vertically suspended platinum cylinder of the usual form receives the deposit of copper. It is not necessary to wait until the cuprous oxide has completely dissolved before closing the circuit.

The test analyses show the remarkable accuracy of the method.

L. DE K.

Rapid Analysis of Blast Furnace Slag. By O. TEXTOR (*J. Anal. and Appl. Chem.*, **7**, 257—262).—The author estimates the silica and alumina in the usual manner by evaporating quickly 0·5 gram of the slag with hydrochloric acid, &c. Whilst this is going on, 1·325 grams of the slag is dissolved in dilute hydrochloric acid, oxidised with a few drops of nitric acid, rendered alkaline with ammonia, and diluted to 530 c.c. After filtering, 200 c.c. (= 0 5 gram slag) is used for the estimation of the calcium by the permanganate process. 250 c.c. is mixed with excess of ammonium oxalate diluted up to 300 c.c., and filtered. 240 c.c. of the filtrate (0·5 gram slag) is precipitated with ammonia and sodium phosphate, and the precipitated ammonium magnesium phosphate washed with dilute ammonia. To save time, the precipitates of the silica, alumina, and magnesium phosphate are washed with the aid of the filter pump, and burnt moist. The alumina may contain traces of iron and the magnesia traces of manganese, but these do not as a rule appreciably affect the results. Sulphur existing as a sulphide may be estimated by treating 0·5 gram of the slag with standard iodine in presence of hydrochloric acid. The excess of iodine is then titrated in the usual manner.

The author does not pretend to great accuracy, but claims to make satisfactory analyses of several samples within a couple of hours.

L. DE K.

Separation of Ferric, Manganous, Calcium, and Magnesium Phosphates. By R. SEELIGER (*Chem. Centr.*, 1894, i, 107—108; from *Pharm. Centr.-Halle* [2], **14**, 685—687).—About 0·3 gram of the mixed phosphates is fused in a platinum crucible with 10 times its bulk of an intimate mixture of sodium carbonate, potassium nitrate, and silica, first over a Bunsen burner, then over a blow-pipe. After cooling, the mass is lixiviated with hot water and any potassium manganate is reduced by passing a few bubbles of hydrogen sulphide. The insoluble matter is dissolved in hydrochloric acid, and, after adding a slight excess of sodium carbonate, mixed with the main liquid. After boiling, the mixture is left for 12 hours, when the bases will have been precipitated as carbonates and

silicates, the phosphoric acid being contained in the alkaline liquid, from which it may be precipitated by magnesium mixture after removing the silica.

The bases are dissolved in hydrochloric acid, the silica rendered insoluble, and the hydrochloric acid filtrate neutralised with ammonia ; the iron and manganese are then precipitated by boiling with sodium acetate and bromine. The filtrate containing the lime and magnesia is first evaporated to a small bulk, in order to remove any remaining traces of manganese, and then treated as usual. The iron is finally separated from the manganese by the acetate method.

<div align="right">L. DE K.</div>

Separation of Nickel and Cobalt in Steel Analyses. By H. v. JÜPTNER (*Chem. Centr.*, 1894, i, 229—230; from *Österr. Zeit. Berg. Hütt.*, **41**, 616).—Fresenius has proved that small quantities of ferric oxide may be completely separated from cobalt and nickel oxides by adding to the hot solution ammonium chloride and excess of ammonia. The precipitate must, however, be freed from impurities by redissolving in hydrochloric acid and reprecipitating with ammonia for a second and third time. The nickel and cobalt are then precipitated by ammonium sulphide, the mixture being finally neutralised with acetic acid. The author fully confirms the accuracy of the method, which gives good results even if the iron exceeds the nickel and cobalt by 200 to 1. If manganese be present, a slight excess of acetic acid should be added. The process also works in presence of alumina.

<div align="right">L. DE K.</div>

Separation of Thorium from the Rare Earths of the Cerium and Yttrium Groups by means of Potassium Nitride. By L. M. DENNIS and F. L. KORTRIGHT (*Amer. Chem. J.*, **16**, 79—83). —The authors find that when potassium nitride, KN_3, is added to a neutral or nearly neutral solution containing thorium and its allied earth metals ; the thorium is precipitated as hydroxide (hydrogen nitride being liberated), whilst the other earth metals remain in solution. The precipitated thorium hydroxide is free from any appreciable quantity of cerium or other earth metals. L. T. T.

Estimation of Organic Matter in Potable Water by means of Permanganate. By P. E. ALESSANDRI (*L'Orosi*, **16**, 397—400). —Kubel's process for the determination of organic matter in water consists in boiling the water for some time with dilute sulphuric acid, and then titrating the boiling liquid with permanganate ; the quantity of organic matter present is taken to be five times the weight of potassium permangante which the water decolorises.

The author proposes to use a standard solution of potassium permanganate containing 0·200 gram per litre for the titration ; it is made up by dissolving the necessary quantity of permanganate in a litre of distilled water. 100 c.c. of the water is boiled for five minutes with 10 c.c. of dilute sulphuric acid, and the standard permanganate is added until the colour is no longer discharged. It is then boiled again for 6—7 minutes, and if the colour disappears, more permanganate is added as before. The number of c.c. of this solution

decolorised by a litre of the water gives directly the number of centigrams of organic matter per litre. A standard solution, prepared by dissolving 0·400 gram of pure crystallised oxalic acid in a litre of water, may be conveniently employed to determine the excess of permanganate added to the water. W. J. P.

Simultaneous Estimation of Carbon, Hydrogen, and Nitrogen. By H. MALFATTI (*Zeit. anal. Chem.*, **32**, 754—761).—The method described is a modification of that of Jannasch and V. Meyer, but is not yet perfected, the results being still somewhat deficient in accuracy. Two tubes, the combustion tube and the reduction tube, are laid side by side in sheet-iron troughs in a Glaser's combustion furnace. One end of the combustion tube is connected with an apparatus for supplying oxygen, consisting of a hard glass tube containing strongly dried potassium chlorate and cupric oxide, a Y-tube containing 50 per cent. potash solution, and serving both as a counter and as a pressure gauge by having its lower limb connected with a mercury reservoir ; a U-tube containing soda lime, calcium chloride, and large plugs of cotton wool, and then a good glass stopcock. The combustion tube contains in order, oxidised copper spirals, the boat with the substance, 16 cm. of reduced copper, obtained by wrapping fine-grained scale copper oxide in copper gauze, and reducing by methylic alcohol, a short plug of silver gauze, and lastly 25 cm. of scale copper oxide. Next in order follow the usual absorption vessels, but between the calcium chloride tube and the potash bulbs there is inserted a Y-tube, whose lower limb is connected with a mercury reservoir by thick walled caoutchouc tubing a meter in length. Following the Liebig's bulbs comes an arrangement constructed from three Y-tubes and a mercury reservoir, by the adjustment of which communication between the combustion and reduction tubes may either be shut off while the air is expelled from the former by oxygen and from the latter by carbonic anhydride, or else the two tubes may be put in communication, and the carbonic anhydride supply be shut off. At the other end of the reduction tube, which is filled with scale copper oxide, all of which except the last 10 cm. is reduced by hydrogen, is attached a Zulkowsky-Ludwig apparatus to receive and measure the nitrogen.

After expelling the air from the combustion tube by oxygen, and from the reduction tube by carbonic anhydride, while heat is applied to the copper oxide, the stopcock, and a clamp between the manometer and the potash bulbs are both closed, and by heating the copper spirals the oxygen in the combustion tube is absorbed. The substance is then heated, and when by its combustion a small positive internal pressure is indicated by the manometer the clamp is opened and the gases allowed to bubble through the Liebig bulbs, the nitrogen passing on into the reduction tube. Oxygen is again admitted, and continued until the substance is completely burnt. During this stage the copper spirals in the combustion tube must be cooled so that the oxygen may sweep all the other gases out of the tube. All the oxygen which passes into the reduction tube is there retained by the copper, and when the cessation of the escape of gas into the Zul

20—2

kowsky apparatus indicates that nothing but pure oxygen is passing from one tube to the other, the communication between them is closed, and the remaining nitrogen expelled by carbonic anhydride. The whole combustion takes about an hour. Blank experiments must be made, since a small volume of uncondensable gas is always obtained, even when nitrogen is not present. On the other hand, traces of the nitrogen oxides escape reduction, and being absorbed in the potash bulbs raise the carbon results. A further error of excess appears to be due to the adhesion of traces of carbon and hydrogen to the porous copper obtained by reduction with methylic alcohol.

M. J. S.

Estimation of the Nitrogen in Benzene Pyridine and Quinoline Derivatives by Kjeldahl's Method. By M. KRÜGER (*Ber.*, **27**, 609—613).—The substance (0·2—0·8 gram) is dissolved in strong sulphuric acid (20 c.c.), contained in a round bottomed flask, heat being applied if necessary. To the cooled solution, potassium dichromate is added, 0·5 gram at a time, to the extent of 0·5 gram more than the amount theoretically necessary for the oxidation. After any evolution of gas has ceased, the flask is placed in a cold water bath, which is then heated to boiling. The flask is kept there until no more gas is evolved, and is then heated on wire gauze with a small flame until the evolution of gas ceases, and the colour of the mixture is a pure green; this indicates the completion of the oxidation, which occupies only 15—30 minutes in all. The ammonia in the mixture is now estimated in the usual way. Good results are obtained with compounds containing no nitrogen, that is directly joined to oxygen or to another nitrogen atom; substances containing such nitrogen have yet to be experimented with. The advantages of this over the other modifications of Kjeldahl's method are (1) the rapidity of the oxidation, and (2) the means of telling when the oxidation is complete.   C. F. B.

Apparatus for the Rapid Estimation of Combustible Gases. By G. G. POND (*Ber.*, **27**, 692—696).—This apparatus is due to Shaw (Philadelphia). It consists of a pump provided with two cylinders, one of fixed, the other of variable, volume, by means of which mixtures of air. or any gas which has to be examined, with a combustible gas can be rapidly and accurately made, so that the resulting mixture contains a known percentage of the added combustible gas. This mixture then passes into a chamber in which it meets with a flame, and, if it explodes, the force of the explosion moves a piston which sounds a bell. In order to rapidly determine the percentage of combustible gas in a sample of air from a coal mine, for example, a mixture of pure air with coal-gas is made which will just exploue and sound the bell of the apparatus. The sample of gas is then substituted for the air, and the amount of coal-gas added diminished until the limit of explosibility is again reached. The difference between the amounts of coal-gas added to reach this limit in the two experiments represents the amount of combustible gas originally present in the sample tested. It is claimed that the apparatus is

sensitive to 0·1 per cent. of combustible gas. The apparatus is also of value for the rapid and exact preparation of mixtures containing known amounts of combustible gas, and may thus be applied to the testing of Davy lamps. A. H.

Estimation of Oil of Turpentine in Alcohol. by J. PERL (*Chem. Zeit.*, **17**. 1851).—Alcohol containing turpentine will stand more or less dilution with water before a turbidity is produced. The more turpentine is present, the less will be the amount of water required. On this fact, the author bases his process for a quantitative estimation of turpentine in denatured spirits. 5 c.c. of the sample is put into a test-glass, and water is added from a burette until a permanent turbidity is produced. 5 c.c. of a 0·5 per cent. solution of turpentine in spirit of the same alcoholic strength as the sample is put into another test-glass, and also titrated. The mixture which consumes most water is the poorest in turpentine, and the author found that 1·1 c.c. of difference in water is equivalent to 0·25 per cent. of turpentine. The author also found that the turpentine cannot be removed by fractional distillation over lime. L. DE K.

Estimation of Alcohol in Wines. By A. BORNTRAEGER (*Zeit. angw. Chem.*, 1894, 108—110).—The author dilutes 100 c.c. of the sample with an equal bulk of water, distils off two-thirds or more, dilutes the distillate to exactly 100 c.c., and takes its specific gravity at 15·5°.

Unless the sample contains more than 0·5 per cent. of volatile acidity, which is rarely the case, it is not necessary to neutralise before distillation. L DE K.

Estimation of Phenol. By L. ZIMMERMANN (*J. Pharm.*, [5], **29**, 105—110).—A modification of Chandelot's method. The aqueous phenol is added to aqueous potassium hypobromite until the latter ceases to discolour starch paper impregnated with potassium iodide and sodium carbonate, the titre of the hypobromite having been found by a similar experiment with a solution of pure phenol of known strength.

If the dilution of the phenol is not greater than 250 c.c. per gram., the result may be calculated at once from the volume used, but if greater than this, a correction is necessary on account of the lack of sensitiveness of the indicator. This correction is proportional to the square of the dilution, so that its values lie on a rectangular parabola, $y = ax^2$, when plotted against it. The value of the constant a, corresponding with 20 c.c. of Chandelot's hypobromite, is 0·00434.

The approximate dilution of the phenol solution of which it is desired to ascertain the strength having been ascertained by titration, the value of the correction y is found from the equation and added to the number of c.c. required to saturate the hypobromite, and the actual dilution then calculated. The numbers quoted show very fair agreement. Tables are given to facilitate the correction.

JN. W.

Solubility of Lead Salts in Sugar Solutions: Estimation of Sugar in Sweet Wines. By J. STERN and P. HIRSCH (*Zeit. angw. Chem.*, 1894, 116—117).—The authors have found that, on adding sodium carbonate to a wine containing excess of lead acetate, the precipitated lead carbonate more or less redissolves in excess of the reagent, and that this is due solely to the presence of levulose.

The excess of lead is, however, completely removed by a current of carbonic anhydride. L. DE K.

Gravimetric Estimation of Pentaglucoses. By E. R. FLINT (*J. Anal. and Appl. Chem.*, 7, 190—194).—The author claims the priority as regards the gravimetric estimation of furfuraldehyde with phenylhydrazine lately proposed by Chalmot. The majority of articles to be tested (plants and fodder articles) contain more or less of glucosides, which, on distillation with hydrochloric acid, yield levulinic acid, acetone, and similar compounds; these pass into the distillate, and would count as furfuraldehyde when the volumetric process is employed. But as these compounds do not give a precipitate with phenylhydrazine, at least in weak solutions, the accuracy of the gravimetric estimation is not influenced by their presence.

The factors for the conversion of the hydrazone into furfuraldehyde, arabinose, xylose, and pentose are respectively: $\times$ 0·538; $\times$ 1·229 + (0·0177); $\times$ 1·031 $-$ (0·001); $\times$ 1·13 + (0·0083). Pentose may be calculated to pentosan by multiplying by 0·88. L. DE K.

Estimation of Pentosans. By E. HOTTER (*Chem. Zeit.*, 17, 1743—1745).—5 grams of the substance containing the pentosan—bran for instance—is distilled with hydrochloric acid of 1·06 sp. gr. until the distillate no longer shows the furfuraldehyde reaction with aniline acetate. The distillate is diluted with hydrochloric acid up to a definite bulk, say 400—500 c.c. and 20—30 c.c., and after the addition of some pyrogallol, is heated in a sealed tube for two hours at 100—110°. The precipitate which forms is collected on a tared filter, washed, and dried at 103°. Its weight, divided by 1·974, gives the amount of furfuraldehyde.

100 parts of pentosan should yield 64 parts of furfuraldehyde, but, owing to secondary reactions, the amount rarely exceeds 50 per cent. L. DE K.

Estimation of Alkalinity and Acidity of Urine. By E. FREUND and G. TOEPFER (*Zeit. physiol. Chem.*, 19, 84—103).—The determination of the reaction of urine is complicated by the presence of various salts, some of which have an acid and others an alkaline reaction. In order to overcome this difficulty, a number of indicators were examined, and it was found that some are differently affected by free acids and alkalis, as distinguished from acid and alkaline salts. The following table gives the chief results.

Reagent.	Colour produced in					
	Alizarin.	Alizarin-blue.	Methyl-orange.	Poirier's-blue.	Brilliant-croceïn.	Phenol-phthaleïn.
Free acid....	Lemon-yellow	Orange	Red	Blue	Red	Colour-less
Monosodium phosphate	Orange	Orange	Orange	Blue	Red	Colour-less
Disodium phosphate	Red	Yellow-green	Yellow	Blue	Red	Pink
Sodium hydrogen carbonate	Red	Yellow-green	Yellow	Blue	Red	Colour-less
Sodium carbonate	Violet	Dark green	Bright yellow	Violet	Brown-red	Red
Trisodium phosphate	Violet	Dark green	Bright yellow	Violet	Brown-red	Red
Free alkali .	Deep violet	Dark green	Bright yellow	Red	Brown	Deep red

The next table shows how the indicators may be used quantitatively with solutions.

Solutions.	Alkalinity.		Acidity.		
	Quantity of decinormal HCl used in c.c.		Quantity of decinormal NaOH in c.c.		
	To decolorise phenol-phtaleïn.	To turn alizarin yellow.	To turn phenol-phthaleïn dark red.	To turn alizarin violet.	To turn Poirier's-blue red.
10 c.c. of 1 per cent. monosodium phosphate	—	0·05	8·35 = 0·98 per cent.	8·3 = 1 per cent.	16·6 = 1 per cent.
10 c.c. of 1 per cent. disodium phosphate	0·1	6·9 = 0·99 per cent.	0·1	0·1	6·95 = 0·99 per cent.
10 c.c. of 1 per cent. trisodium phosphate	6·3 = 1·05 per cent.	12·3 = 1 per cent.	—	—	0·05
10 c.c. of 1 per cent. sodium hydrogen carbonate	0·1	11·6 = 0·99 per cent.	2·0	2·0	11·8 = 1 per cent.
10 c.c. of 1 per cent. sodium carbonate	9·4 = 1 per cent.	18·3 = 0·988 per cent.	—	—	0·1

Sodium carbonate thus gives a measure of acidity, and trisodium phosphate of alkalinity. Disodium phosphate and sodium hydrogen carbonate have an acidity to one reagent equal to their alkalinity to another.

Mixtures of various salts were next subjected to titration ; by using different indicators, a very accurate estimation of the proportions present was obtained.

Three examples of the method as applied to urine are given. The headings of the table being the same as in the last, the results obtained were :—

1. 10 c.c. of afternoon urine	—	10·1	0·6	0·6	12·65
2. 10 c.c. of urine before meal	—	3·7	1·4	1·4	7·4
3. 10 c.c. of urine after meal	—	7·2	1·2	1·4	10·8

The first specimen of urine gave an alkaline reaction to litmus paper, but, nevertheless, contained a high amount of acid salts, whereas the second and third specimens, which were from the same individual, were acid to litmus paper, but still contained alkaline salts. It will be further noticed in these two specimens that the values for the acid salts were unchanged by the meal, but that the alkaline salts were nearly doubled. W. D. H.

Estimation of the Acidity of Gastric Juice. By G. TOEPFER (*Zeit. physiol. Chem.*, **19**, 104—122).—The object of the present research was to furnish the clinical observer with a ready method by which titration could be employed to indicate not only the total acidity of the contents of the stomach but also the proportion of the various acids to which this is due. The plan of the investigation resembles that described in the preceding abstract. A large number of indicators were tried, first with acids, then with mixtures of these with albumin, and, finally, with artificial digestive mixtures, and also with the contents of the stomach. The following method was adopted. The reagents necessary are, (1) a decinormal solution of sodium hydroxide ; (2) a 1 per cent. alcoholic solution of phenolphthaleïn ; (3) a 1 per cent. aqueous solution of sodium alizarinsulphonate ; and (4) a 0·5 per cent. alcoholic solution of dimethylamidoazobenzene.

5 to 10 c.c. of the gastric mixture is placed in each of three beakers ; to the first, two drops of phenolphthaleïn solution is added, and the sodium hydroxide run in from a burette until a quite dark-red is obtained, not deepened, by further addition of alkali.

To the second portion, three or four drops of the alizarin solution is added, and titration again performed, until the first appearance of a pure violet tint (similar to that given by 5 c.c. of 1 per cent. sodium carbonate with the four drops of the alizarin solution) indicates the end reaction.

To the third portion, three or four drops of the dimethylamidoazobenzene solution are added, and titration performed until the last trace of red has disappeared, and is replaced by yellow.

The third titration gives the value of the free hydrochloric acid.

The difference between the first and second titration gives the value of the loosely combined hydrochloric acid. The second titration gives the total acidity. The total acidity *minus* the free and loosely combined hydrochloric acid gives the amount of acidity due to other factors, especially organic acids and acid salts.　　　　W. D. H.

Preservation of Milk for Estimation of Fat. By M. WEIBULL (*Exper. Stat. Record.*, **5**, 536—537; from *Svensk. kemisk. Tidskr.*, 1893). —Potassium permanganate (60 to 100 milligrams) is added to about 20 c.c. of milk which will then keep for several months at 64—72° F. Sufficient permanganate is added to produce a dark-brown colour, the milk being shaken until it is completely dissolved; the colour dis-appears in a few days when more permanganate is added. Compara-tive analyses with fresh milk and with milk kept 6 to 56 days, gave results in which the greatest difference was 0·1 per cent., whilst in eight out of eleven cases the difference was 0·05 per cent. or less.

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Estimation of Fat in Bread. By M. WEIBULL (*Exper. Stat. Record.*, **5**, 520; from *Svensk. kemisk. Tidskr.*, 1892, No. 5).—Direct extraction of bread with ether, however long continued, gives too low results, owing to the fat being enclosed by the starch and dextrin. The results were lower than those obtained from the flour from which the bread was made. The following method is given. The dry powdered bread (1—3 grams) is boiled for an hour with water (15—20 c.c.) containing 10 drops of dilute sulphuric acid, stirring occasionally. The solution is then neutralised with marble free from fat, and the thick solution transferred to a fat-free filter paper, the beaker being wiped out with absorbent cotton. The paper and cotton are dried at 100° and extracted with dry ether for 10 hours.

Comparative estimations of the fat in bread and in the flour from which it was made gave perfectly concordant results by this method.

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Estimation of Asparagine. By J. LEWINSKY (*Chem. Centr.*, 1894, i, 53—54).—See this vol. ii, 216.

Estimation of Emetine in Radix Ipecacuanhæ. By C. C. KELLER (*Chem. Centr.*, 1894, i, 236—238; from *Schweiz. Woch. Pharm.*, **31**, 473—477).—*1st method.* 12 grams of the powdered air-dried drug is extracted in a suitable apparatus with ether to remove the fat. It is then transferred to a counterpoised 200 c.c. flask and mixed with more ether, so that the weight of the latter shall be 90 grams. 30 grams of chloroform is then added, and after five minutes 10 c.c. of a 10 per cent. ammonia solution, and the whole shaken vigorously for half an hour. 10 c.c. of water is now intro-duced, and after again shaking for a few minutes, 100 c.c. of the clear solution is poured off; the ether and chloroform are removed by distillation, the residue is washed a few times with a small quantity of ether, then dried for 15 minutes in the water bath, weighed, and

titrated with N/10 hydrochloric acid, 1 c.c. of which equals 0·0254 gram of emetine.

2nd method.   12 grams of the powder is put into a dry bottle and repeatedly shaken with 90 grams of ether and 30 grams of chloroform.   After 5 minutes, 10 c.c. of ammonia is added, and after half an hour 10 c.c. of water; 100 c.c. of the clear liquid is then poured off and shaken in a separating funnel three times in succession with 25, 15, and 10 c.c. of 1 per cent. hydrochloric acid.   The acid layer is then made alkaline with ammonia and agitated twice with 50 c.c. of a mixture of 3 parts of chloroform and 2 parts of ether.   The solvent is removed by distillation and the residue finally titrated as before.   L. DE K.

Modification of Grandeau's Method for the Estimation of Humus. By H. A. HUSTON and W. F. McBRIDE (*Exper. Stat. Record,* **5,** 559—560; from *Indiana Stat. Bull.,* No. 46, 67—79).—When investigating the black soils of Indiana, it was found that in some cases the extraction with ammonia by Grandeau's method required over a week.   There was also a difficulty of repeating experiments under the same conditions since the percolation through duplicate samples of the same soil was not uniform as to rate.   In the modified method, a definite amount of soil is kept in contact with a definite volume of ammonia for a fixed time.   The soil, after being washed as usual with acid and water, is washed into a 500 c.c. stoppered cylinder with 500 c.c. of ammonia.   After being shaken, the cylinder is kept for 24 hours in an inclined position (without letting the liquid touch the stopper), and for 12 hours in an upright position, to allow the soil to settle before taking out an aliquot part of the solution.   The results were much higher than those obtained by the original method, but soils extracted by the old method give further quantities of humus when extracted a second time, making the results nearly the same when 2 per cent. ammonia is employed.

In soils not peaty, the strength of the ammonia makes practically no difference in the results, whilst with peaty soils comparatively little difference is found when the strength is 2 per cent. or more.   The adoption of a standard temperature for the digestion is recommended.

The results are much more concordant than those obtained by the original method.

The large number of phosphoric acid and potash determinations made in the ash of the extracted humus did not show any relation between the amounts of humus and of phosphoric acid and potash respectively.   There is no evidence to show that either substance is associated with humus before its extraction.   N. H. M.

General and Physical Chemistry.

Molecular Refraction. By H. JAHN and G. MÖLLER (*Zeit. physikal. Chem.*, **13**, 385—397).—A continuation of the researches of Landolt and Jahn (Abstr., 1893, ii, 57). The method used was the determination of the dielectric constant, this being effected by comparison with that of metaxylene. The refraction also was observed for the H_α, H_β, H_γ, and Na lines, and the constants calculated in Cauchy's formula, $\mu = A + \dfrac{B}{\lambda^2}$. In the substances observed, the values for $\sqrt{\kappa}$ (κ = dielectric constant) and A did not agree, the former being in all cases too high, *i.e.*, the dispersion is anomalous.

	$\sqrt{\kappa}$.	A.
Amylic chloride	2·5284	1·3987
Tertiary amylic chloride......	3·0737	1·3956
Amylic bromide.............	2·4853	1·4317
Ethylenic chloride...........	3·259	1·4342
Ethylenic bromide...........	2·1940	1·5207
Bromobenzene	2·3274	1·5339
Chlorobenzene	2·3504	1·5003
Benzylic chloride............	2·6291	1·5146
Chlorotoluene	2·3064	1·5003
Amylenic bromide...........	2·3648	1·4920

The dispersion-free molecular refraction is also calculated by the formula $M\dfrac{\kappa - 1}{\kappa - 2}\cdot\dfrac{1}{d}$. As thus determined, the chloro- and bromo- compounds of univalent radicles appear to have approximately the same molecular refraction, although the numbers are different for hydrogen light. The displacement of hydrogen by chlorine in the benzene ring is attended by a great increase; also the displacement in the straight chain or in substituted benzenes, such as aniline, &c. The same holds in the case of the displacement by bromine, but as the numbers for chlorine or bromine differ greatly in the different series, it follows that the dispersion-free molecular refraction is not entirely additive, but is markedly dependent on the constitution. The entrance of two bromine atoms causes the same increase as that of one. Acetic, propionic, butyric, valeric, and isobutyric acids were also examined; in this case again the value obtained for the molecular refraction of acetic acid appears abnormally high. The dielectric constants for mixtures of different liquids was also observed in order to test whether the property was simply additive in mixtures; in many cases this appeared to be the case, but in others the found and calculated values do not agree.

L. M. J.

Line Spectrum of Oxygen. By M. EISIG (*Ann. Phys. Chem.*, [2], **51**, 747—760).—The measurements by different observers of the

line spectrum of oxygen have been confined to single portions of the spectrum, have been made by different methods, and making use only of small dispersions. In order to obtain a complete set of comparative results, the author has therefore undertaken a careful examination of the complete oxygen spectrum, with the use of the concave grating employed by Kayser and Runge in their researches on the line spectra of the elements. The results are given in tabular form, and compared with those of Schuster, of Deslandres, of Trowbridge and Hutchins, and of Hartley and Adeney. No relationships between the reciprocals of the wave lengths, such as those obtained by Kayser and Runge in the case of other elements, are in any way evident, and a comparison with the solar spectrum also shows an absence of general coincidence between the lines of the oxygen spectrum and that of the sun.   H. C.

Polarisation of a Thin Metal Partition in a Voltameter. By J. DANIEL (*Phil. Mag.*, [5], **37**, 185—201, and 288—300).—When a thin metal partition is introduced between the poles of a voltameter, gases are evolved at its surface, but if the thickness of the partition is below a certain limit, the current passes without evolution of gas and without evident polarisation. The author finds that the "critical thickness," that is, the least thickness of partition through which the current passes without polarisation, is 0·00009 mm. for gold, 0·00015 mm. for platinum, and 0·0005 mm. for aluminium, with a small current and a good conducting electrolyte. The "upper critical limit," that is, the smallest thickness for which the polarisation is the same as for very thick plates, is about 0·004 mm. under the above conditions. Between the critical limits, the polarisation increases with the thickness.

Special experiments indicated that in the case of copper sulphate solution, the passage of the current was not accompanied by the passage of copper ions through the gold-leaf partition, but rather that the copper sulphate itself diffused bodily through the membrane.

                                                                    J. W.

Dielectric Constants and Chemical Equilibrium. By W. NERNST (*Zeit. physikal. Chem.*, **13**, 531—536).—As the energy of an electrically charged system is lowered when placed in a medium of higher dielectric capacity, the author points out that there is hence an attractive force on electric points towards the medium with the higher capacity. From this he deduces, by considering the ions as electrically charged points, that the greater the dielectric constant, κ, of a medium, the greater will be the electric dissociation of a dissolved substance. Data for verification are few, but the known facts support this view, thus:—

	κ.	Electric dissociation.
Gases	1·0	Not at ordinary temperatures.
Benzene	2·3	Very slight; traces.
Alcohol	25·0	Distinct.
Water	80·0	Very strong.

Experiments also on the dissociation of hydrogen chloride gave:

benzene, xylene, and hexane, very slight; ether, slightly stronger; then isobutylic alcohol, ethylic alcohol, and methylic alcohol, the order being the same as that of the dielectric capacity. Many organic acids contain molecular complexes, which decompose first into simple molecules and then into ions. The decomposition would also probably follow this law. This action is observable in the following order, according to the measurements of Eijkman and Beckmann; hydro-carbons ($\kappa = 2\cdot2—2\cdot4$); carbon bisulphide ($\kappa = 2\cdot6$); chloroform (κ ?); ether ($\kappa = 4\cdot4$); ethereal salts ($\kappa = 6—9$); alcohols ($\kappa = 16—33$); acids (κ ?); and water ($\kappa = 80$). A short indication is also given of a method for the simple and accurate determination of the constants.   L. M. J.

Minimum Electromotive Force necessary for Electrolysis. By M. Le Blanc (*Compt. rend.*, **118**, 702—707; and by Berthelot (*ibid.*, 707—709).—A question of priority (compare this vol., i', 223).   C. H. B.

Formation of Floating Metallic Films by Electrolysis. By F. Mylius and O. Fromm (*Ann. Phys. Chem.*, [2], **51**, 593—621).—During the electrolysis of a concentrated zinc sulphate solution, it was observed that the cathode wire became surrounded by a film of metallic zinc floating upon the surface of the solution, the film increasing gradually to a considerable size. A somewhat similar observation has been made by F. Kohlrausch in the case of the electrolysis of a solution of silver chloride in ammonia, and the authors have therefore been led to study the conditions under which the formation of such films take place. Experiments made with zinc sulphate and ammoniacal silver chloride show that the two principal necessary conditions are, an impure state of the surface of the solution, and the presence of oxygen in the atmosphere above the solution. If the surface is perfectly clean, formation of a film is not observed, whilst on the other hand, the addition of the smallest trace of any oily impurity, such as turpentine, which will float upon the surface, favours the film formation. If the air above the liquid is replaced by hydrogen, carbonic anhydride, or nitrogen, the film is not formed. Observations with both the zinc and silver films point to the presence of some trace of oxidised metal in the film, and if the surface of the solution is covered with an oil that has been completely freed from dissolved oxygen, the film is not formed. In other cases, the formation of a film below the surface of the liquid, as at the boundary between the solution and a heavy oil like chloroform, is possible. Films were also obtained from copper, cadmium, cobalt, iron, and antimony solutions. When the copper solution is treated with a solution of sulphur, in a mixture of benzene and carbon bisulphide, the surface film consists chiefly of cuprous sulphide, and a solution of iodine in benzene on the surface of silver sulphate gives rise to the formation of a silver iodide film.   H. C.

Changes of Temperature caused by Contact of Liquids with Powdered Silica, &c. By G. Gore (*Phil. Mag.*, [5], **37**, 306—316).—Finely divided silica was brought into contact with

10 per cent. solutions of various substances, and the resulting rise of temperature noted ; this rise varied with the nature of the substance dissolved, and increased with the fineness of the powder. Finely divided calcium carbonate, alumina, barium sulphate, and other substances were also tested, with similar results. J. W.

Thermal Expansions of Solutions in Organic Solvents. By G. TAMMANN and W. HIRSCHBERG (*Zeit. physikal. Chem.*, 13, 543—549). —It had been previously pointed out that the isobars of solutions at atmospheric pressure correspond with those of the solvent, if the latter are considered for a somewhat higher pressure (this vol., ii, 224) ; data were forthcoming in the case of water, but for other liquids hardly any were available. The authors' aim was therefore to verify experimentally the above conclusion. The expansions of various solutions in alcohol, ether, benzene, and carbon bisulphide were determined, the method used was the dilatometric, and the volumes were observed at four temperatures, 0°, 10°, 20°, and 30°; the results showing that the solutions were in all cases less expansible than the solvent. The expansions of alcohol and ether for pressures from 1 to 500 atmospheres were taken from the researches of Amagat (*Ann. Chem. Phys.* [6], **29**, 518). Solutions of calcium chloride, sodium iodide, potassium acetate, mercuric chloride, potassium iodide, ammonium bromide, ammonium nitrate, ferric chloride, iodine, tartaric acid, salicylic acid, ethylic benzoate, borneol, and acetanilide in alcohol; and of benzoic acid, salicylic acid, naphthalene, and mercuric chloride in ether were examined, and for various concentrations, the pressure at which the expansion of the solvent agreed with that of the solution being determined.

The pressure Δ divided by the concentration was approximately constant for different concentrations, the value sometimes increasing and sometimes decreasing with the temperature ; this value, $\Delta\kappa/m$, is noticeably less than the values for solutions in water, in which solvent also it is greater for electrolytes than for non-electrolytes.

L. M. J.

Melting Point Determinations at a Red Heat. By V. MEYER and W. RIDDLE (*Ber.*, **27**, 766).—The authors have determined the melting points of certain salts with a larger (platinum) air thermometer than that previously used in determining the solidifying points (this vol., ii, 6). The new results agree roughly with the old ones, except in the case of sodium carbonate, the melting point of which is now found to be considerably lower than that of potassium carbonate, although still higher than those of sodium chloride or sulphate. C. F. B.

Apparatus for Facilitating the Boiling of Liquids. By V. GERNHARDT (*Ber.*, **27**, 964—965).—An ordinary flask is fitted at the bottom with a short rod of red Jena fusible glass, in a similar manner to the platinum wire in Beckmann's boiling point apparatus ; the advantages of the red glass are, its cheapness and freedom from risk of fracture on heating or cooling, whilst, owing to its high conductivity

and greater mass, the liquid is as readily heated as when platinum is employed. J. B. T.

Separation of Three Liquids by Fractional Distillation. By F. R. BARRELL, G. L. THOMAS, and S. YOUNG (*Phil. Mag.*, [5], **37**, 8—31).—The authors calculate curves representing graphically the progress of the distillation of three liquids on the assumption that the proportion of the three substances in the vapour forming the instantaneous distillate is the same as that of the weights of the three substances in the residue in the still, each weight being multiplied by a suitable constant, which is roughly proportional to the vapour pressure of the corresponding liquid.

To test the validity of the results arrived at, a mixture of 200 c.c. of methylic acetate, 250 c.c. of ethylic acetate, and 200 c.c. of propylic acetate, was distilled from a flask provided with a still-head 1 metre long. After 26 preliminary fractionations, the liquid had been divided into two series of fractions, one series containing practically only ethylic and methylic acetates, the other series ethylic and propylic acetates. Six further fractionations separated the individual ethereal salts. The quantities of pure methylic, ethylic, and propylic acetates finally obtained were respectively equal to 48, 53, and 72 per cent. of the quantities originally taken. J. W.

Law of corresponding Boiling Points. By U. DÜHRING (*Zeit. physikal. Chem.*, **13**, 492—499).—The paper is a claim for priority of enunciation of the law of corresponding boiling points, particularly with respect to E. Colot's and S. Young's claims. The author bases his claims on the expression of the law as $t' = \gamma + qt$, in a publication in 1878, and in *Ann. Phys. Chem.*, [2], **11**, 164 (1880), in which expression, t' and t are the boiling points of two liquids at the same pressure, and γ and q are constants. L. M. J.

Van der Waals's Corresponding States. By S. YOUNG (*Phil. Mag.*, [5], **37**, 1—8; compare Abstr., 1893, ii, 63).—From his collected data for the corresponding pressures, volumes, and temperatures of 22 liquids in contact with their saturated vapours, the author shows that van der Waal's generalisations regarding " corresponding " states are approximately true within certain groups of substances, those examined by him falling into four chief series, namely,

I. Benzene, its halogen derivatives, carbon tetrachloride, stannic chloride, ether.

II. Methylic, ethylic, and propylic alcohols (methylic alcohol differing, however, considerably from the others).

III. Acetic acid.

IV. Ten ethereal salts.

The alcohols and acetic acid diverge most from the other substances, this being probably due to the molecular aggregation shown to exist in these liquids by Ramsay and Shields. J. W.

Pressure of Saturated Vapours. By K. D. KRAEVITCH (*Phil. Mag.*, [5], **37**, 38—90).—The author finds that the following formula

may be used for calculating the vapour pressure of liquids at different temperatures with close approximation.

$$\text{Log } \frac{p}{p_0} = -\frac{c - c_1}{\text{AD}}\left(\log \frac{\text{T}}{\text{T}_0} - m\frac{\text{T} - \text{T}_0}{\text{T}}\right) + \frac{mr_0}{\text{AD}}\left(\frac{1}{\text{T}_0} - \frac{1}{\text{T}}\right).$$

Here p and p_0 are the pressures at the absolute temperatures T and T_0; c and c_1 the specific heat of the vapour at constant volume and constant pressure; A the thermal equivalent of work; D the gas constant; r_0 the latent heat of vaporisation, and m the modulus of the decadic logarithms.

The difference $c - c_1$ is supposed to be constant throughout the ranges of temperature considered.

A comparison of the calculated values with experimental data is given for a large number of substances.　　　　　　　J. W.

Apparatus for Determining the Specific Gravity of Soft Fats. By Z. Zawalkiewicz (*Monatsh.*, **15**, 132—138).—The apparatus consists of a weighing bottle with two narrow necks. Of these, one comes from the base, and through it the just-molten fat enters from a reservoir placed above; the excess of fat passing out from the other neck into a small chamber. By this means the bottle is completely filled with fat, and air-bubbles are excluded. In order to control the temperature, the bottle and reservoirs are placed in a specially-arranged glass vessel which allows of the melting of the fat and the subsequent slow cooling to the point at which it is desired to determine the specific gravity. The paper is accompanied by a sketch of the apparatus, and gives numbers obtained for various fats.　　　　　　　G. T. M.

Determination of Small Dissociation Tensions of Hydrated Salts. By C. E. Linebarger (*Zeit. physikal. Chem.*, **13**, 500—508). —The author points out that if a substance is dissociated by a liquid into soluble and insoluble components, the partial pressure of the former, when equilibrium occurs, must be equal to the dissociation tension of the substance, and if, further, for this constituent the partial pressure is known at different concentrations and temperatures, then the dissociation tension may be determined by finding the quantity of the soluble constituent dissolved. A number of hydrated salts in ether are thus examined. A table is first given connecting the quantity of water dissolved with the lowering of the boiling point of the ether. By means of Nernst's formula

$$p = 39\frac{mx}{1\cdot315 \times 0\cdot58},$$

(where p = partial pressure, m = quantity of water, and x proportion of double mols. dissociated) a table is next set out giving the partial pressure of water for every $0\cdot01°$ lowering of the boiling point of ether. Determinations are then recorded of this lowering by the addition of several hydrated salts, namely, cupric sulphate, strontium chloride, magnesium sulphate, zinc sulphate, barium chloride, man-

ganese sulphate, and ferrous sulphate, and the partial pressure cf the dissolved water then calculated. This is equal to the dissociation tension of the salt.

In the first four cases, the results are compared with those of Frowein (Abstr., 1888, 337), and are seen to be quite concordant. In the cases, however, of barium chloride and ferrous sulphate, no trustworthy results could be obtained. L. M. J.

Dissociation of Potassium Triiodide in Aqueous Solution.
By A. A. JAKOVKIN (*Zeit. physikal. Chem.*, **13**, 539—542).—The dissociation can be studied by allowing a solution of iodine in potassium iodide solution to remain in contact with carbon bisulphide until equilibrium is reached; any iodine formed by the dissociation (nonelectrolytic) must divide itself between the two solvents in a constant ratio independent of concentration. As the partition ratio for carbon bisulphide and water is 410 : 1, the quantity of free iodine in the solution can be estimated by analysing the carbon bisulphide.

The constant of dissociation according to the equilibrium equation $KI_3 \rightleftarrows KI + I_2$ is calculated by the formula $k = \dfrac{(a - 1 + x)x}{v(1 - x)}$, where a is the ratio of mols. of KI to mols. I_2, and x is the ratio of free to total iodine, v being the volume per gram molecule of iodine. From 32 experiments with varying concentrations of iodine and of potassium iodide, a mean value $k = 1683 \times 10^{-6}$ was found, the individual numbers varying from 1577 to 1808, with a mean difference of about 2 per cent. If the value of k be calculated for other equilibrium equations, e.g., $KI_5 \rightleftarrows KI + 2I_2$, the value of k varies within very wide limits, 10180 to 461, $\times 10^{-8}$. From this the author concludes that there are certainly KI_3 molecules in this solution, and that the law of Henry extends to undoubtedly chemical and partly dissociated solutions. L. M. J.

The Hydrolysis of Weak Acids and Bases. By S. ARRHENIUS
(*Zeit. physikal. Chem.*, **13**, 407—411).—The author examines some of the results of Lellmann and Schliemann (Abstr., 1893, ii, 407) which the latter had considered were not in accordance with the dissociation theory as at present understood. The author, therefore, calculates from the basis of this theory the ratios of the extinction coefficients of solutions of helianthin in acetic, propionic, hydroxyisobutyric, chloracetic, and trichloracetic acids, and compares them with the observed numbers of Lellmann. The results are shown in

Acetic Propionic·		Hydroxyisobutyric Acetic ·		Monochloracetic Hydroxyisobutyric·		Trichloracetic Monochloracetic·	
Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1·08	1·04	1·12	1·16	1·12	1·08	1·08	1·05
1·20	1·06	1·25	1·28	1·23	1·16	1·11	1·07
1·37	1·09	1·40	1·44	1·32	1·28	1·14	1·09

the table (p. 271), the horizontal line corresponding with three different concentrations in ratio $1 : 4 : 16$, the upper line being the strongest. L. M. J.

General Law of Solubility of Normal Substances. By H. LE CHATELIER (*Compt. rend.*, **118**, 638—641).—If the latent heat of solution of a substance is considered as equal to its latent heat of fusion, the author shows that the following relationship may be developed from established laws respecting the behaviour of solutions :—

$$0{\cdot}002 \log s - \frac{L}{t} + \frac{L}{t_0} = 0,$$

where s is the concentration of the dissolved substance expressed as the number of molecules of this substance in 1 mol. of the solution, L is the latent heat of fusion, t_0 the melting point of the dissolved substance, and t the solidifying point of the solution. As the equation contains no term relating to the solvent, the conclusion is evident that the curve of solubility of a given substance in any solvent will always be of the same form. H. C.

Mutual Solubility of Salts. By H. LE CHATELIER (*Compt. rend.*, **118**, 709—713).—In the determination of the solubility of salts one in another, or, what comes to the same thing, of the fusing points of saline mixtures, three general cases may be distinguished.

1. The salts solidify to form isomorphous mixtures of variable composition.

2. Each salt solidifies separately from the mixture.

3. The two salts combine and solidify as a compound of definite composition.

Cases of the first kind have already been considered by the author, and also by Küster (Abstr., 1892, 396), and in the present paper instances of the second kind are recorded. The solubilities of sodium chloride and of lithium sulphate in various salts were measured by determining the fusing points of the saline mixtures. The following table gives the results.

Substance.	Solvent. $s =$	Melting points.				
		1.	0·9.	0·8.	0·7.	0·6.
NaCl	Na_2CO_3	778	755	—	718	692
,, ...	$Pb(NO_3)_2$	—	762	742	710	—
,, ...	$BaCl_2$	—	758	740	—	690
,, ...	Calculated......	—	758	738	717	694
Li_2SO_4........	$CaSO_4$	830	750	675	—	—
,, ...	Li_2CO_3	—	745	667	580	—
,, ...	Na_2SO_4	—	750	680	620	—
,, ...	Calculated......	—	741	661	580	—

s in this table is the concentration of the dissolved substance, and the calculated values were obtained, making use of the formula developed by the author (see preceding abstract). The latent heats of fusion per gram molecule of the dissolved salts deduced from these results are 12·6 cal. for NaCl and 5·68 cal. for Li_2SO_4. That the solubility is independent of the nature of the solvent, as predicted (*loc. cit.*), is in so far confirmed by these determinations. H. C.

Solubility of Mercuric and Sodium Chlorides in Ethylic Acetate. By C. E. LINEBARGER (*Amer. Chem. J.*, **16**, 214—216).— Continuing his work on this subject (Abstr., 1893, ii, 450), the author gives a table and a curve of the solubility of mercuric chloride in ethylic acetate in the presence of varing proportions of sodium chloride. Determining the separate solubilities of the two salts, 100 mols. of ethylic acetate at 40° dissolved 16 mols. of mercuric chloride, but only 0·037 mol. of sodium chloride; when, however, a mixture of the chlorides was treated. a solution was obtained which contained 40 mols. mercuric chloride, and 20 mols. of sodium chloride, to 100 mols. of ethylic acetate. The influence of the sodium chloride is first to somewhat reduce the solubility of the mercuric chloride, such influence being greatest when two molecules of sodium chloride have gone into solution in 100 mols. of the solvent (the solubility of the mercuric chloride being then 12 mols. in 100). The solubility of both salts then increases, at first slowly, then more rapidly.

L. T. T.

Saturated Solutions. By R. LÖWENHERZ (*Zeit. physikal. Chem.*, **13**, 459—491).—The paper contains researches on the saturated solutions containing potassium and magnesium chlorides and sulphates in all their possible combinations. The results are expressed graphically by taking the four edges which meet at the corner of a regular octa-hedron as the axis, and marking along them, in order, the solubility of potassic sulphate, potassic chloride, magnesium chloride, and mag-nesium sulphate. Upon each of the faces between two of these edges, for instance, the $K_2SO_4 : K_2Cl_2$ are then lines representing the effects of the addition of one of these salts on the solubility of the other, so that the point where the two lines meet represents the composition of the solution saturated by both salts. Lines similarly drawn from these points into the space of the solid angle represent the effect of the other salts on the saturation composition of these solutions, so that the space is ultimately closed by a surface divided into fields which give the composition of solutions saturated with the salts KCl; K_2SO_4; $MgCl_2$; $MgSO_4,6H_2O$; $MgSO_4,7H_2O$; carnallite; and schönite. The lines separating the fields correspond with solutions saturated by two of these salts, and the points where the lines meet represent solutions saturated by three substances which are present as solids in contact with the solutions. Some of the data were already known, but most had to be experimentally deter-mined, as the solubility of $MgCl_2$; $MgSO_4,6H_2O$ and $MgCl_2,6H_2O$; $MgSO_4,7H_2O$ and $MgSO_4,6H_2O$; $MgCl_2,6H_2O$ and $MgCl_2,KCl,6H_2O$; carnallite and KCl; and the composition of solutions saturated with three salts. From the figure thus obtained, it is possible to calculate

what substance will first crystallise out from a solution of any given composition, and what substance next, &c. A number of experiments performed gave in all cases results which agreed with those thus deduced. L. M. J.

Molecular Weight in Solid Solutions. By F. W. KÜSTER (*Zeit. physikal. Chem.*, **13**, 445—458).—In order to determine with what molecular weight ether is dissolved in caoutchouc, the author studies the lowering of the freezing point of water, owing to ether in the presence of caoutchouc. The substances employed were carefully purified, and the lowering of the freezing point by ether alone was first determined. A figure of the apparatus employed is given, being a Beckmann thermometer in a well-jacketed flask. The caoutchouc was found to exercise no effect on the freezing point of the water, and in the case of water, ether and caoutchouc equilibrium was found to occur in about $1\frac{1}{2}$ hours. A number of experiments are then recorded, made, at the freezing point of the solution, with 50 c.c. of water, 5 c.c. of ether, and varying quantities of caoutchouc. From the lowering of the freezing point, the quantity of ether dissolved in the water is calculated, and hence that dissolved in the caoutchouc. The percentage volume concentration in the two solvents is thus known. If C_k be this concentration in the caoutchouc and C_w in the water, the results gave $C_k/C_w = 1\cdot21$; $1\cdot55$; $1\cdot69$; $1\cdot81$, and $\sqrt{C_k}/C_w = 0\cdot435$; $0\cdot466$; $0\cdot473$; $0\cdot469$; the higher numbers corresponding with the smaller quantity of caoutchouc. It thus appears that the caoutchouc molecules contain abnormal molecules of ether, and from the approximate constancy of $\sqrt{C_k}/C_w$ probably double molecules. The next series of experiments were at a temperature of 18—16°, and were made with 50 c.c. water, 10 grams caoutchouc, and quantities of ether varying from 1 to 14 c.c. The ratio of C_k/C_w varied from $3\cdot10$ to $5\cdot36$, and that of $\sqrt{C_k}/C_w$ from $1\cdot58$ to $0\cdot76$. The increase with concentration is, as would be expected, slower than at low temperatures, while the decrease of the numbers $\sqrt{C_k}/C_w$ indicates a smaller number of double molecules in the more dilute solutions, and also that they become very numerous in higher concentrations. The ratio C_k/C_w is calculated as 2 8 for infinite dilution, where all molecules are simple. The ratio of the number of the *simple* molecules in the two solvents, however, must be independent of the concentration. Hence the value $2\cdot8\ C_w = C_k$ gives the concentration of simple molecules in the caoutchouc, and the difference $C_k - 2\cdot8\ C_w = C''_k$, the concentration of the complex molecules. If they are really double molecules, the equation $(C'_k)^2 = KC''_k$ should obtain. The values of the ratio $C'_k/\sqrt{C''_k}$ are deduced and are approximately constant, varying, in 11 experiments, from $5\cdot3$ to $5\cdot8$. A series of experiments performed at 0° are similarly treated, and for low concentration the value $\sqrt{C_k}/C''_k$ only varies between $3\cdot0$ and $3\cdot3$. For very high concentrations, however, it decreases considerably. L. M. J.

Velocity of Hydrolysis of some Ethereal Salts. By A. DE HEMPTINNE (*Zeit. physikal. Chem.*, **13**, 561—569).—The author deter-

mines the velocity of hydrolysis of 11 of the lower ethereal salts, the reaction being induced by hydrochloric acid in a N/20 solution of the salt, at a temperature of 25°. The values for K, calculated by the formula $K = \dfrac{1}{t} \log \dfrac{A}{A - x}$ are given in the table.

	Acetate.	Ratio.	Propionate.	Ratio.	Butyrate.
Methylic ..	0·001432	1·074	0·001538	1·797	0·0008560
Ratio ..	0·9670		0·9736		
Ethylic....	0·001481	1·066	0·001580	1·744	0·0009061
Ratio ..	1·016		1·004		
Propylic ..	0·001458	1·078	0·001573	1·781	0·000883

Ethylic isobutyrate, 0·000889; ethylic valerate, 0·000312.

The values calculated for the same units as Reicher's numbers may be obtained from the above by multiplying by 4·624. It is seen from the equality of the ratios for the same series, that if the velocities for one series are known, those for another can be calculated from that of one of its members. The nature of both acid and alcohol is seen to affect the rate. Comparison made with Reicher's numbers for hydrolysis by sodium hydroxide show that the action of the hydroxyl ions is greater than that of the hydrogen ions. The author also describes some experiments made to discover whether the acid exerted any catalytic action in the gaseous state. A gaseous mixture of ethylic acetate and hydrogen chloride was kept for two hours at a temperature of 210°, when it was found that 15 per cent. of the salt was hydrolysed. The author does not consider, however, this can yet be stated to be due to free ions. L. M. J.

Endothermic Reactions effected by Mechanical Force. By W. Spring (*Zeit. anorg. Chem.*, **6**, 176).—Carey Lea ignores the author's work when he claims (this vol., ii, 85) that, before himself, no one had accomplished the conversion of mechanical into chemical energy. Eleven years ago the author expressly wrote (*Bull. Acad. Belg.*, [3], **5**):—"The facts to which I have just called attention prove conclusively that it is possible to cause substances to react chemically by means of mechanical energy alone." C. F. B.

Phases and Conditions of Chemical Change. By V. H. Veley (*Phil. Mag.*, [5], **37**, 165—184).—The author distinguishes four stages through which chemical actions pass, namely, (1) a period of commencement, (2) of inertness, or reluctance followed by acceleration, (3) of constancy, (4) of diminution of velocity; and gives examples illustrating this division. He then proceeds to discuss the nature of chemical change, and the cause of its commencement, criticising adversely Armstrong's reversed electrolysis theory, Arrhenius' theory of electrolytic dissociation, and the notion of nascent action. J. W.

Expenditure of Energy Equivalent to the Chemical Action of Light. By G. Lemoine (*Compt. rend.*, **118**, 525—528).—In studying the action of oxalic acid on ferric salts (Abstr., 1893, ii, 405), no account was taken of the possible influence of light on the

course of the reaction. It has now been ascertained, experimentally, that this influence is practically inappreciable, and that light probably plays no part beyond that of aiding in inducing the reaction in question.   H. C.

Employment of Electricity to follow the Phases of certain Chemical Reactions. By J. GARNIER (*Compt. rend.*, 118, 588—589).—A mixture of nickel oxide and wood charcoal was placed in an earthenware tube, closed by two plugs of soft steel, by which the mixture was compressed. The two steel plugs were placed in an electric circuit, and the earthen tube, supported horizontally, was heated in a small reverberatory furnace. The resistance of the powder in the tube was at first extremely high, but gradually became less and less, until it became almost nil. It then increased again, finally becoming very high. The decrease of resistance corresponds with the gradual reduction of the oxide, the reduction being complete at the moment when the resistance was almost nil; as the nickel became carburetted, however, the resistance increased.

In a similar experiment, with a mixture of copper, iron, and nickel oxides and wood charcoal, the successive phases of reduction were indicated by the variations in the resistance. In the same manner, the process of refining might be followed, and the method has the advantage that the readings of the ammeters and voltmeters can be made at a point removed from the position of the furnace, &c.
                                                      C. H. B.

Accurate Determination of Atomic Weights, using Silver as a Secondary Standard. By G. HINRICHS (*Compt. rend.*, 118, 528—531).—Comparing the results obtained by Dumas, Stas, and Cooke for the atomic weight of sulphur, referred to that of silver taken as 108, the author maintains that the atomic weight found is a function of the amount of silver taken. The following table of comparison is given.

	No. of experiments.	Wt. of Ag in grams.	At. wt. found.
Cooke	2	1·0	32·004
Dumas......	2	10·0	31·998
Dumas......	3	30·7	32·028
Stas	7	164·8	32·084

If η is the atomic weight found for sulphur, and ω the weight of silver used, $\eta = 0.001\ \omega - 0.000003\ \omega^2$. Similar results are obtained for chlorine, bromine, and the other elements whose atomic weights were determined by Dumas and Stas.

The author applies his method of limits to these results, and for $\omega = 0$ finds the atomic weights Cl = 35·5, Br = 80, I = 127, and S = 32 exactly when Ag is taken as 108.   H. C.

Crystalline Structure. By W. NERNST (*Zeit. physikal. Chem.*, 13, 537—538).—A reply to an observation of Retgers (*Zeit. physikal.*

Chem., **12**, 621), in which the author claims to have been misquoted by the former, and contests, although without discussion, the accuracy of his statement, that several amorphous bodies behave, in certain of their physical properties, as if composed of crystalline fragments too small for direct perception. L. M. J.

Inorganic Chemistry.

Occurrence of Hydrogen Peroxide in the Air. By L. Ilosvay DE N. Ilosva (*Ber.*, **27**, 920—925).—In reply to Schöne (this vol., ii, 88), the author maintains that, owing to the presence of nitrogen peroxide as a constant constituent of the atmosphere, the evidence hitherto brought forward to establish the presence of ozone and hydrogen peroxide in the air or in rain water, is insufficient. The oxidising effects which have been observed are all due to this agent, and when this is removed, no evidence of the presence of any other oxidising agent more powerful than free oxygen can be found.

A. H.

Hydrogen Peroxide in the Atmosphere. By E. Schöne (*Zeit. anal. Chem.*, **33**, 137—184).—This discussion of the results of Ilosvay de Ilosva covers precisely the same ground as that communicated to the *Ber.* (this vol., ii, 88), but with more minuteness of detail.

M. J. S.

Ratio of the Atomic Weights of Oxygen and Hydrogen. By J. Thomsen (*Zeit. physikal. Chem.*, **13**, 398—406).—The method employed was an indirect one, in which the ratio of the molecular weights of hydrogen chloride and ammonia was determined. If the ratio $NH_3/HCl = \gamma$, then it follows that the atomic weight of hydrogen, in terms of Cl and N, is given by the equation $H = \dfrac{\gamma Cl - N}{3 - \gamma}$

Pure dry hydrogen chloride was first passed into pure distilled water, and the increase in weight found; it was then neutralised as nearly as possible by pure ammonia, and the increase of weight again observed. The liquid was finally exactly neutralised by a standard solution, which contained 0·01703 gram of hydrogen chloride per gram. The mean of 17 experiments, with quantities of water varying from 100 to 200 grams, and from 4 to 19·4 grams of hydrogen chloride gave the ratio $HCl/NH_3 = 2·14087$, with a probable error of $+0·00009$, or, when corrected for vacuum weighings, $HCl/NH_3 = 2·13934 \pm 0·00009$ and $\gamma = 0·467433 \pm 0·000019$.

The atomic weights of hydrogen are then calculated from the values of Stas, Ostwald, and Von der Plaats, for chlorine and nitrogen (referred to O = 16).

	Stas.	Ostwald.	Von der Plaats.
Cl	35·457	35·4529	35·4565
N	14·044	14·0410	14·0519
H	0·9989	0·99946	0·9959

The probable error is given in the ratios $d\mathrm{H} = 14\cdot4\ d\gamma$, $\alpha\mathrm{H} = 0\cdot185\ d\mathrm{Cl}$, and $d\mathrm{H} = 0\cdot395\ d\mathrm{N}$.

If Stas' value for chlorine, and Ostwald's value for nitrogen, be taken, the ratio of the weights of oxygen and hydrogen becomes exactly 16 : 1, which is, therefore, as near the true ratio as the accuracy of present data allows. L. M. J.

Phenomena of Oxidation-and Chemical Properties of Gases. By F. C. PHILLIPS (*Amer. Chem. J.*, **16**, 163—187, 235—254).—See this vol., ii, 293, 294.

Stability and Preparation of Free Hydroxylamine. By C. A. LOBRY DE BRUYN (*Ber.*, **27**, 967—970).—A number of specimens of hydroxylamine, prepared by the author in September, 1891, have been analysed; one, which had been kept in a cellar, solidified at 28·5°, contained 93 per cent. of hydroxylamine and a trace of ammonia, but no nitrous acid; pure hydroxylamine solidifies at 33°. Hydroxylamine is tolerably stable at temperatures up to 15°, the decomposition proceeds gradually, ammonia, nitrous acid, and hyponitrous acid are first formed, and these, together with the unaltered hydroxylamine, interact with production of nitrogen and nitrous oxide. Hydroxylamine hyponitrite is probably too unstable to exist, as the nitrite decomposes above 20° in methylic alcoholic solution; only one of the above specimens of hydroxylamine contained a trace of hyponitrous acid. The alkalinity of the glass vessels in which the hydroxylamine is preserved greatly facilitates its decomposition.

The paper contains a number of details regarding the preparation of hydroxylamine, and a discussion of Brühl's communication (this vol., i, 9) on the subject. J. B. T.

Composition and Heat of Formation of the Hydrate of Nitrous Oxide. By VILLARD (*Compt. rend.*, **118**, 646—649).—The hydrate of nitrous oxide (Abstr., 1888, 1020) was formed from water and liquid nitrous oxide in a glass tube, and the latter was cooled below 0° and the excess of gas allowed to escape. The composition of the hydrate was determined by measuring the volume of gas given off on heating, and five experiments gave results varying between $N_2O,5\cdot9H_2O$ and $N_2O,6\cdot44H_2O$, and hence, in all probability, the true composition is $N_2O,6H_2O$. Experiments made by measuring the volume of the liquid nitrous oxide before combination with a known quantity of water, and the volume of the oxide in excess, gave $N_2O,6\cdot6H_2O$ and $N_2O,6\cdot3H_2O$.

Direct measurements in the calorimeter gave the following results :—

Formation of hydrate from the dissolved gas (water,
  1 gram) .... = 77·8 cal.
Dissolution of the corresponding gas.............. = 57·5 ,,
Formation of the hydrate from the gas and water .. = 139·0 ,,

The crystals of the hydrate have no action on polarised light, and show distinct octahedral terminations; they, therefore, seem to belong to the regular system. C. H. B.

Carbon Boride. By H. Moissan (*Compt. rend.*, **118**, 556—560). —Carbon boride is formed when the electric arc is allowed to pass between two carbons agglomerated by means of a solution of boric acid and aluminium silicate, or when boron is placed in the electric arc, but much larger quantities can be obtained by heating a mixture of 66 parts of amorphous boron and 12 parts of carbon from sugar in the electric furnace for six or seven minutes with a current of 250—300 ampères and 70 volts. It forms a black, graphitoidal mass with a brilliant fracture, and after prolonged treatment with fuming nitric acid, followed by potassium chlorate and nitric acid, a crystalline powder remains.

Another method is to add an excess of boron and carbon to some iron and heat the mixture in the electric furnace. A regulus with a very brilliant fracture is obtained, and after treatment with aqua regia a residue is left, which consists almost entirely of carbon boride in badly defined crystals, which can be further purified by means of nitric acid and potassium chlorate.

Owing to the ease with which iron dissolves boron, better results are obtained by heating the mixture of boron and carbon with silver or copper; with the former the product is pure, but is confusedly crystalline; with the latter the crystals are well defined. 15 grams of the mixture of carbon and boron is heated with 150 grams of copper in the electrical furnace for six or seven minutes with a current of 350 ampères and 70 volts. The product is treated with nitric acid, and afterwards with the acid and potassium chlorate.

Boron carbide, prepared by any of these methods, has the composition CBr_6, and forms brilliant, black crystals of sp. gr. 2·51. It is attacked by chlorine below 1000° without incandescence, but it is not affected by bromine or iodine, or by sulphur, at the softening point of glass, or by phosphorus or nitrogen at 1200°. It is not attacked by boiling acids, or when heated in sealed tubes at 150° with chromic acid, fuming nitric acid, or a concentrated solution of iodic acid. When heated in oxygen at 500°, no carbonic anhydride is formed, but at 1000° the carbide burns slowly and with greater difficulty than the diamond, yielding carbonic anhydride, and a black residue surrounded by fused boric anhydride. At a dull red heat, carbon boride is attacked by potassium hydroxide, or by a fused mixture of potassium and sodium carbonates.

Carbon boride is very friable, but is also very hard, and although slightly softer than the diamond, it can be used to polish the latter, and produces very distinct facettes.　　　　　　　　　　　C. H. B.

Potassium Double Salts of Hypophosphoric acid. By C. Bansa (*Zeit. anorg. Chem.*, **6**, 128—142 and 143—160).—The sodium hydrogen salt of the acid, $Na_2H_2P_2O_6$, was first prepared by immersing sticks of phosphorus, all but about 1 cm. of each, in a 25 per cent. solution of sodium acetate; it separated in crystalline crusts. It was converted, by means of barium chloride, into the barium hydrogen salt, and this, by means of potassium sulphate, into the potassium hydrogen salt. By adding, to a strong solution of the latter, solutions of salts of the heavy metals, amorphous precipitates were first

obtained, consisting of the normal hypophosphates of the heavy metals, but these gradually took on a crystalline form, becoming converted into the acid potassium double salts. The latter were dried on a porous plate and analysed at once; they were not washed, as water decomposes them. By neutralising a solution of potassium hydrogen hypophosphate with caustic potash, a solution of normal potassium hypophosphate was obtained; on adding solutions of heavy metals to this, amorphous precipitates of the normal hypophosphates were at first formed, but gradually became converted into the normal potassium double salts. The acid double salts, when heated in the air, seem to form first pyrophosphates and then metaphosphates, but hydrogen is evolved, and some hydrogen phosphide.

Acid Double Salts.—Those of *nickel* (green), *cobalt* (pink), *zinc*, and *copper* (blue), with potassium, form crystals of the rhombic system, and are isomorphous, having the composition $M''H_2P_2O_6, 3K_2H_2P_2O_6 + 15H_2O$. The *cadmium*, $CdH_2P_2O_6, K_2H_2P_2O_6 + 2\frac{1}{2}H_2O$, and the *manganese*, $MnH_2P_2O_6, K_2H_2P_2O_6 + 3H_2O$, potassium double salts are colourless.

Normal Double Salts.—The *nickel*, $NiK_2P_2O_6 + 6H_2O$, and *cobalt*, $CoK_2P_2O_6 + 5H_2O$, potassium double salts were prepared; they are respectively green and pink. The *potassium sodium* double salt, $K_2Na_2P_2O_6 + 9H_2O$, can be obtained by neutralising the potassium hydrogen salt with sodium carbonate; the same substance is obtained when the sodium hydrogen salt is neutralised with potassium carbonate. It forms colourless crystals belonging to the rhombic system, $a : b : c = 1\ 0728 : 1 : 1·0845$.   C. F. B.

Action of Nitrogen, Nitrous Oxide, and Nitric Oxide on Alkali Amides. By A. JOANNIS (*Compt. rend.*, **118**, 713—716).—Nitrogen has no action on solutions of the alkali metals in liquid ammonia.

When nitrous oxide acts on the solution, the principal reaction is $N_2O + N_2H_6K_2 = KNH_2 + NH_3 + KOH + N_2$. If, however, the passage of the gas is continued after the liquid has been decolorised, the reaction, $2NH_2K + N_2O = N_3K + KOH + NH_3$, takes place. By reason of this reaction, a small quantity of the nitride N_3K is formed even before the solution has been decolorised.

Sodammonium behaves in a similar manner, and it is noteworthy that the formation of the nitride N_3Na proves that the product of the first action is $NaNH_2 + NaOH$, and is not the compound NH_3Na_2O, which is obtained by the action of oxygen on sodammonium.

Nitric oxide is absorbed by a solution of sodammonium or potassammonium in liquefied ammonia, the blue colour disappearing and a pinkish, gelatinous product being formed, which, when the ammonia has evaporated, remains as an amorphous powder. The products thus obtained are sodium hyponitrite and potassium hyponitrite respectively.   C. H. B.

Note by Abstractor.—The formation of the nitride N_3Na from solid sodamide and gaseous nitrous oxide has already been observed by W. Wislicenus (Abstr., 1892, 1151).   C. H. B.

Atomic Weight of Barium. By T. W. RICHARDS (*Zeit. anorg. Chem.*, **6**, 89—127).—Two series of determinations were made with great care. In the first, the ratio $2AgCl : BaCl_2$ was determined, the barium chloride employed having been (1) ignited in air and corrected for oxide and carbonate formed, (2) ignited in hydrogen chloride, or (3) crystallised and merely dried. The barium chloride was precipitated with excess of a solution of silver in nitric acid, and the precipitate collected and weighed. In the second series, the ratio $2Ag : BaCl_2$ was determined, the barium chloride being precipitated by a slight excess of the solution of silver, and the excess of the latter determined in one of four different ways.

Assuming the atomic weights $Cl = 35\cdot456$, $H = 1\cdot0075$, $Ag = 107\cdot930$, the two series give respectively the values $137\cdot439$ (10 experiments; maximum deviation $+0\cdot042$ and $-0\cdot022$) and $137\cdot440$ (14 experiments; maximum deviation $+0\cdot042$ and $-0\cdot057$). Including the results obtained with barium bromide (Abstr., 1893, ii, 463), the mean result is $137\cdot434$; omitting certain determinations made by methods which are deemed less trustworthy, we have $137\cdot441$. It is sufficient to take as the final result $Ba = 137\cdot44$.   C. F. B.

Specific Gravity of Fused Magnesium Oxide. By H. MOISSAN (*Compt. rend.*, **118**, 506—507).—The sp. gr. of magnesium oxide increases with the temperature at which it has been heated. Ditte obtained the following values: at $350°$, $3\cdot1932$; at a dull red heat, $3\cdot2482$, and at a bright red heat, $3\cdot5699$. The author has obtained the following values at higher temperatures. After heating in a wind furnace for ten hours, $3\cdot577$; after heating in the electric furnace for two hours, $3\cdot589$; after fusing in the electric furnace, $3\cdot654$. It would seem that the polymerisation of the magnesium oxide continues up to its melting point.   C. H. B.

Crystallised Normal Magnesium Carbonate. By K. KIPPENBERGER (*Zeit. anorg. Chem.*, **6**, 177—194).—If freshly precipitated magnesium carbonate, made by mixing equivalent amounts of magnesium sulphate and sodium carbonate, is shaken with a solution of potassium hydrogen carbonate at the ordinary temperature, much of the magnesium carbonate dissolves, and crystallises out of the filtered solution after a time; the separation is ended in 24 hours. The same occurs if sodium hydrogen carbonate is used; it dissolves relatively more of the magnesium carbonate, but the crystals obtained are smaller. Solutions containing respectively $67\cdot5$ grams of potassium and $12\cdot96$ grams of sodium hydrogen carbonate per litre dissolved, respectively, $18\cdot73$ and $9\cdot95$ grams of magnesium carbonate. The crystals have the composition $4MgCO_3 + 15H_2O$; after four weeks in dry air, or 15 hours in a vacuum desiccator over sulphuric acid, they have the composition $2MgCO_3 + 5\frac{1}{2}$ (or $6)H_2O$; after heating at $170°$ the composition $MgCO_3 + \frac{1}{6}$ (or $\frac{1}{3})H_2O$. The reaction is, according to the author, that a double sesquicarbonate of magnesium and the alkali metal is formed, and that this afterwards decomposes, magnesium carbonate being precipitated, and carbonic anhydride liberated, which latter regenerates the alkali bicarbonate with the alkali sesquicarbonate now present.

Alkali bicarbonates do not dissolve calcium carbonate or ferric hydroxide, and upon this fact the author bases a technical process for the preparation of pure magnesium carbonate from dolomite, magnesite, and bitterspar, and from kainite or carnallite liquors. The mineral is powdered, dissolved in commercial hydrochloric acid, and the iron oxidised by warming gently with a little nitric acid. The solution is then precipitated with sodium carbonate in slight excess, the filtered precipitate shaken with a sufficiently strong solution of alkali bicarbonate, and the solution filtered after the lapse of 20 minutes, and set aside to crystallise. The mother-liquor can be used again and again for the extraction.   C. F. B.

Thallium Hypophosphates. By A. JOLY (*Compt. rend.*, **118**, 649—650).—*Dithallous hypophosphate*, $Tl_2H_2P_2O_6$. is obtained by exactly neutralising a solution of hypophosphoric acid with thallium carbonate in presence of methyl-orange, or by the action of a boiling aqueous solution of thallium sulphate on monobarium hypophosphate. It forms anhydrous, colourless, transparent, and highly refractive monoclinic prisms. When heated somewhat below 200°, it melts suddenly and is converted into phosphate, and if heated above 200°, hydrogen phospide is given off.

Tetrathallous hypophosphate, $Tl_4P_2O_6$, is almost insoluble in cold water and is prepared by mixing boiling aqueous solutions of thallium sulphate and disodium hypophosphate in the calculated proportions. It separates in anhydrous, small, very slender, colourless, silky needles, and may be washed with cold water, and recrystallised from boiling water. When heated at about 250°, it suddenly liquefies with development of heat, but without loss of weight, and becomes black, being converted into a mixture of thallium metaphosphate and reduced thallium, $Tl_4P_2O_6 = 2TlPO_3 + Tl_2$. If the salt is quite dry no hydrogen phosphide is given off.

When exposed to direct sunlight, tetrathallous hypophosphate becomes indigo-blue at the surface, as if the same change were produced as under the influence of heat.   C. H. B.

Molecular Weight of Ferric Chloride. By P. T. MULLER (*Compt. rend.*, **118**, 644—646).—The author has determined, by Raoult's ebullioscopic method, the molecular weight of anhydrous ferric chloride in solution in alcohol and ether. The results are given in the following table, p being the weight of ferric chloride in 100 grams of the solvent, E the rise in the boiling point, and M the molecular weight given by the expression $M = Kp/E$, in which K is a constant with the value 11·5 in the case of alcohol and 21·1 in the case of ether.

Alcoholic Solution.			*Ethereal Solution.*		
p.	E.	M.	*p.*	E.	M.
2·860	0·21°	156·62	11·467	1·21°	200·0
4·416	0·31	163·8	6·985	0·86	171·3
6·556	0·47	160·41	2·888	0·42	145·0
10·132	0·72	161·83	2·006	0·28	151·1

It is clear that when dissolved in boiling alcohol or ether, the molecular weight of ferric chloride is represented by the formula $FeCl_3$. In the ethereal solution the molecular weight is lower the more dilute the solution. C. H. B.

Alloys of Nickel and Iron. By F. Osmond (*Compt. rend.*, **118**, 532—534).—The alloys investigated had the following composition :—

	A.	C.	E.	G.	J.	K.	L.	M.	N.
Carbon....	0·19	0·13	0·19	0·17	0·23	0·19	0·16	0·14	0·16
Silicon	0·31	0·23	0·20	0·28	0·24	0·27	0·30	0·38	0·31
Manganese.	0·79	0·72	0·65	0·68	0·93	0·93	1·00	0·86	1·08
Nickel	0·27	0·94	3·82	7·65	15·48	19·64	24·51	29·07	49·65

A shows three points of transformation, namely at 775—765°, 715—695° and 645—635°, and C shows three points, at 755—745°, 695—685°, and 625—615°. In the case of E, the second and third points coincide at 645—635°, whilst the first falls to 565—550; in G, the second and third points coincide at 515—505°, and the first point either disappears or coincides with the other two. As the proportion of nickel increases, the single point at which heat is developed during cooling becomes lower and lower ; it is 130—120° in the case of J, 85—65° in the case of K, and the change is not complete even at the ordinary temperature in the case of L. M shows no appreeiable development of heat, but N shows a point at 380—340°, from its position and feeble intensity, however, this seems to correspond with the known point of transformation of nickel.

The rate of cooling and the initial temperature have much less influence than in the case of hard steels or of alloys of iron with tungsten and chromium.

The appearance of magnetic properties seems to coincide with the second point. The alloys from A to L are strongly magnetic, but from G the magnetism decreases and M is almost non-magnetic. In N, however, the magnetism reappears. L is non-magnetic above 50°, but becomes magnetic between this temperature and 0°.

In J, K, and L the allotropic change is accompanied by a great increase in hardness, and the hardness corresponds with magnetic polarity as in the case of tempered steel. Both hardness and polarity seem to correspond with incomplete transformation.

C. H. B.

Purification of Thorium Oxide. By P. Jannasch (*Zeit. anorg. Chem.*, **6**, 175).—The method of preparing pure thorium oxide, regarded as new by Böttinger (this vol., ii, 238), had already been used by the author, Locke and Lesinsky (this vol., ii, 52).

C. F. B.

Compounds of Thorium Oxide with Phosphoric and Vanadic acids. By C. Volck (*Zeit. anorg. Chem.*, **6**, 161—167).—By adding a rather dilute solution of orthophosphoric acid to a dilute solution of thorium chloride, a white flocculent precipitate is obtained soluble in acids ; it has, when dried at 100°, the composition $ThO_2,P_2O_5 + 2H_2O$ or $Th(HPO_4)_2 + H_2O$, and loses all its water at 220°. If

sodium phosphate is used to precipitate the thorium, the precipitate is always contaminated with sodium.

By adding an 8 per cent. solution of ammonium metavandate to a dilute solution of thallium chloride, a greenish-yellow precipitate is obtained, soluble in acids; when dried at $100°$, it has the composition $ThO_2,V_2O_5 + 6H_2O$ or $Th(HVO_4)_2 + 5H_2O$.   C. F. B.

Mineralogical Chemistry.

Minerals of the Serpentine, Chlorite, and Mica Group. By R. BRAUNS (*Jahrb. f. Min.*, 1894, i, Mem., 205—244).—The author adversely criticises the method of investigation employed by F. W. Clarke and E. A. Schneider (Abstr., 1893, ii, 78) in their researches on the constitution of the natural silicates. He is of opinion that the hydrogen chloride gas used was not absolutely dry, and that that fact militated against the value of the theoretical views of Clarke and Schneider. His own theory is that the entire chlorite group is formed of several families existing in morphotropic relations. The individual families, whose representatives may be taken to be clinochlore, pennine, leuchtenbergite, and corundophilite, consist of several members existing in isomorphous relations. These members in isomorphous admixture invariably form minerals, a part of the magnesia being replaced by ferrous oxide, and of the alumina by ferric oxide, or by chromic oxide, &c. The micas, he believes, also form a morphotropic group. B. H. B.

Meerschaum from Bosnia. By M. KIŠPATIĆ (*Jahrb. f. Min.*, 1894, i, Ref., 443, from *Verhandl. k. k. geol. Reichsanst.*, 1893, 241—242).—At Ljubić-planina near Prnjavor, in Bosnia, meerschaum occurs with impure magnesite, and has the following composition.

SiO_2.	MgO.	Fe_2O_3.	H_2O.	Total.
61·09	25·87	2·59	10·47	100·02

B. H. B.

Chemical Investigation of Topaz. By P. JANNASCH and J. LOCKE (*Zeit. anorg. Chem.*, **6**, 168—173).—This paper describes only the determination of the amount of water contained in crystals of topaz from different localities; this ranged from 0·80—2·69 per cent. A horizontal tube was used, with a bulb near one end, and a layer of dry lead oxide in the longer limb, which was connected with a calcium chloride tube. The powdered mineral was mixed with dry lead oxide, and the mixture placed in the bulb and fused, while a current of dry air was aspirated through the apparatus. The increase of weight of the calcium chloride tube gave the amount of water in the mineral. C. F. B.

Artificial Preparation of Beryl. By H. TRAUBE (*Jahrb. f. Min.*, 1894, i, Mem., 275—276).—The author has obtained crystallised

beryl by a method similar to that employed by him in the preparation of zinc silicate. It consisted in precipitating the silicate in an amorphous state from an aqueous solution, and then melting it with boric anhydride at a high temperature. On adding sodium silicate to a solution containing 3 mols. of $BeSO_4$ and 1 mol. of $Al_2(SO_4)_3$, a copious precipitate is obtained, having the composition $Be_3Al_2Si_9O_{18} + xH_2O$. Six grams of the carefully dried precipitate was mixed with 2·5 grams of boric anhydride in a platinum crucible, and heated for three days to a temperature of 1700°. The product was distinctly crystalline, colourless hexagonal tablets and prisms being detected. Analysis yielded

SiO_2.	Al_2O_3.	BeO.	Total.
67·38	18·61	13·48	99·47

Beryl is thus a metasilicate, as had previously been assumed. It may possibly be regarded as a double salt, $3BeSiO_3 + Al_2Si_3O_9 = Be_3Al_2Si_6O_{18}$. B. H. B.

Chemical Composition of Pyrope and other Garnets. By C. v. JOHN (*Jahrb. f. Min.*, 1894, i, Ref., 436—437, from *Jahrb. k. k. geol. Reichsanst.*, **43**, 53—62).—The author has analysed the typical pyrope from Meronitz (I), and from Triblitz (II), with the following results.

	SiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.
I.	41·72	21·63	1·98	1·61	7·53	0·13	4·34
II.	41·99	21·25	1·80	1·84	7·88	0·38	5·38

	MgO.	Total.	Sp. gr.
I.	21·42	100·36	3·70
II.	20·12	100·64	3·71

He also gives the results of analyses of garnets from Australia, from India, from Olaphian, from Williamsburg, New York, and from Rezbánya, in Hungary. B. H. B.

Paramelaphyre. By H. LORETZ (*Jahrb. f. Min.*, 1894, i, Ref., 459; from *Jahrb. preuss. geol. Landesanst.*, 1893, 129—137).—The eruptive rock, occurring at Gotteskopf, near Ilmenau, in Thuringia, described by E. E. Schmid, in 1881, as paramelaphyre, belongs to the porphyrite group. The holo-crystalline groundmass consists of plagioclase and orthoclase, with occasionally quartz. Magnetite, or titaniferous magnetite and apatite, are always present. In the groundmass, porphyrite crystals of biotite occur, with, more rarely, plagioclase and, in unaltered specimens, augite. Five analyses of the rock are given. B. H. B.

Eklogites and Amphibole Rocks of Styria. By J. A. IPPEN (*Jahrb. f. Min.*, 1894, i, Ref., 461—462; from *Mitt. naturw. Ver. f. Steiermark*, 1893, 56—97).—The eklogites of the Bacher mountains are essentially mixtures of omphacite and garnet, containing also horn-

blende, zoicite, zircon, and quartz.   Carefully isolated omphacite
gave on analysis the following results.

	SiO₂.	Al₂O₃.	FeO.	CaO.	MgO.	Na₂O.	K₂O.	Ignition.	Total.
I.	51·14	4·35	4·60	26·65	11·28	1·20	0·46	0·36	100·04
II.	51·28	4·28	5·21	18·51	16·58	1·73	0·85	1·20	99 64

I. Omphacite from the eklogite of St. Veit; sp. gr., 3·215.   II.
Omphacite from the eklogite of Tainach.   B. H. B.

Physiological Chemistry.

**Digestibility of Normal Oats and of Oats heated at 100° :
Effect of Feeding with Oats on the Weight and Composition
of Bones.** By H. WEISKE (*Landw. Versuchs-Stat.*, **43**, 457—475).—
It is frequently assumed that foods are rendered less digestible
through heating, owing to the conversion of soluble albumin into the
insoluble form, and the generally diminished digestibility of brown hay,
pressed fodder, &c., as compared with that of normal food, is attri-
buted to the high temperature to which such fodder has been exposed.
Morgan (*Landw. Jahrb.*, **21**, 69) showed that diffusive residues
become considerably less digestible when heated at 125—130°, but that
a temperature of 75° was without effect.   Gabriel's results (*ibid.*, **38**,
69) indicated that steam at 140° diminished the amount of digestible
protein in lupins by about 20 per cent., and that the proteïds in a
substance which was originally almost entirely digested, lost one-
eighth of their digestibility when heated for eight hours at 130—140°
(compare Stutzer, *Bied. Centr.*, 1889, 209).   The question is next con-
sidered from another side, namely, the effect of heat on the rate of
digestion (compare Stutzer, *Landw. Versuchs-Stat.*, **40**, 173, 311, and
317; Abstr., 1891, 752; 1892, 1367).   It is pointed out that an in-
crease of the time required for digestion is not necessarily a disad-
vantage, and that substances may be too quickly digested.   So that
artificial digestion experiments are not sufficient, but must be supple-
mented by experiments with animals (compare Neumeister, *Lehrb.
Physiol. Chem.*, **1**, 305; Atwater, *Zeit. Biol.*, [2], 1888, 139 ;
Chittenden and Cummins, Abstr., 1885, 569; and Popoff, Abstr., 1890,
1450).

In the author's experiments, two rabbits of the same litter were
fed daily with oats (8 grams), the one with normal oats, the other
with oats which had been heated at 100° successively in dry air and
in moist air (48 hours).   After 22 days, the feeding was reversed
for a period of 18 days.   During the first period, the weight of the
rabbits remained almost constant, and both rabbits digested their
food about equally well.   The same results were obtained during
the second period of the experiment, so that it may be assumed
that the heated and normal oats have about the same value.   It is,

however, suggested, that geese, &c., would digest less heated than normal corn, as the corn passes through the whole digesting canal in a few hours. In the second period, the digestion-coefficient for proteïn was less than in the first (with both rabbits). The feeding was continued for some days longer, until the rabbits began to leave portions uneaten, when they were killed and analysed. Two more rabbits of the same litter, which had been fed on hay and a little oats (and which had grown much more than those fed on hay alone) were also killed and analysed for comparison.

With the exception of the amount of fat in the bones, all the results (total amounts) obtained with the normally fed rabbits (hay and oats) are much higher than the others. This confirms the previous results, that oats without food giving an alkaline ash, has influence on the development of the bones. As regards the percentage results, it is shown, as in the previous experiments, that the bones, but not the teeth, are affected. The analysis of the bones indicates that there is more organic matter and less mineral in the bones of rabbits fed with oats alone than with those fed with hay and oats. In the ash itself, only the phosphoric and carbonic anhydrides vary to any extent, the phosphoric anhydride being slightly higher in the bones of rabbits fed with oats alone, and the carbonic anhydride being highest in the normally fed rabbits.

The rabbits were nine months old at the commencement of the experiment, and therefore completely developed (compare Wildt, *Landw. Versuchs-Stat.*, **15**, 404). It is supposed that the continued feeding with oats alone caused a diminution of the skeleton, and especially of mineral matter. This is due, as previously stated, not to insufficient lime in the food, but chiefly to its acid nature.

N. H. M.

Composition of the Skeletons of Animals of the Same Kind and Age, but of Different Weights. By H. Weiske (*Landw. Versuchs-Stat.*, **43**, 475—480).—Three rabbits of the same litter were fed alike on hay and oats, and killed when they were 107 days old. They weighed 890, 1050, aad 1480 grams respectively. The rabbits were analysed, and the results compared with those previously obtained with two other rabbits (also 107 days old), which had grown normally, and weighed 2020 and 1890 grams. The total weights of the skeletons and the percentage of live weight, and the composition of the skeletons, are given in tables.

The results show that in poorly developed rabbits the size and weight of the bones are less than in normally developed rabbits, and that the bones contain less minerals. As regards the teeth, the difference in weight is much less, and there is practically no difference in composition.   N. H. M.

Influence of Subdivision of Food on Metabolism. By C. Adrian (*Zeit. physiol. Chem.*, **19**, 123—136; compare Abstr., 1893, ii, 383).—The present experiments, carried out on a dog, confirm on the whole the author's previous conclusions. The beneficial result of a subdivision of the food (flesh) into several meals is not due to the

increased consumption of proteïd, as the total nitrogen in the excreta is the same as when the diet is all given in one large meal; but sub-division of the food lessens the amount of proteïd which is decomposed into products of putrefaction, which are of no use in nutrition. The proteïd absorbed as such is therefore increased.   W. D. H.

Metabolism in Italian Peasants. By P. ALBERTONI and I. NOVI (*Pflüger's Archiv*, **56**, 213—246).—The research was carried out on a man, woman, and boy belonging to an Italian peasant family, both in winter and summer. The results consist very largely of analytical tables of the food taken, with its heat value, and the output in urine and fæces.

Recent writers have urged that equilibrium is possible on smaller quantities of nitrogenous food than the older physiologists thought necessary. It is pointed out that individual idiosyncrasy must be taken into account before laying down a general rule, and this is emphasised by the fact that different results were obtained in the three subjects of experiment.   W. D. H.

Bile and Metabolism. By C. VOIT (*Zeit. Biol.*, **30**, 523—561).—This is a republication of experiments performed on two dogs many years ago.

The amount of bile and the time of maximum secretion were investigated under a large number of conditions—different diets, and so forth. Other excreta were in many cases analysed simultaneously. Full references are given to previous work on the same subject. The paper consists largely of elaborate tables and details, and general conclusions appear difficult to find. As previous observers state, most bile is secreted when the proteïd in the food is abundant; the amount also appears to vary with the discharge of carbonic anhydride in the expired air.   W. D. H.

Sulphur in Human Muscle. By H. SCHULZ (*Pflüger's Archiv.*, **56**, 203—212).—Previous analyses of the amount of sulphur in animal tissues (this vol., ii, 58) are here supplemented by experiments on human muscle. The average gives 1·1 per cent. of the dried, or 0·25 per cent. of the fresh tissue. Prolonged putrefaction causes little or no diminution in the amount. Traces only of this sulphur are contained as sulphate, but the amount of sulphate appears to be somewhat increased during the process of drying at 110°.
                                        W. D. H.

Estimation of the Volume of the Blood Corpuscles and Plasma. By E. BIERNACKI (*Zeit. physiol. Chem.*, **19**, 179—224).—Hamburger (Abstr., 1893, ii, 426) has pointed out that so-called "physiological saline solution" is by no means an indifferent fluid to red blood corpuscles, and thus Bleibtreu's method (*ibid.*, 331) for the estimation of the relationship between plasma and corpuscles is untrustworthy. The present communication points out another source of error in the use of the centrifugal machine.

Defibrinated blood yields more sediment than blood in which coagulation has been prevented by an oxalate. The amount of sedi-

ment is also increased by diluting it with "physiological saline solution." These differences appear to be due to the changes in the size of the corpuscles (shrinkage and swelling), and also as to whether or not they are collected into rouleaux.

The use of the centrifugal machine appears to exaggerate these differences, and in both defibrinated and oxalated blood (normal and pathological) the sediment is lessened as compared with specimens where the corpuscles are allowed to settle without the use of centrifugal force. W. D. H.

Fibrin and Fibrinogen. By J. J. FREDERIKSE (*Zeit. physiol. Chem.*, **19**, 143—163).—The view of blood coagulation urged by Pekelharing, Lilienfeld, and others, that fibrin originates by the interaction of fibrinogen and a calcium compound of nucleo-albumin, is urged.

The presence or absence of serum-globulin in such mixtures makes no difference in the amount of fibrin formed.

Hammarsten's statement that the fibrinogen molecule is split into fibrin or coagulated proteïd and a soluble globulin by the action of heat or of fibrin ferment is confirmed. The same decomposition of the fibrinogen molecule is brought about by the action of dilute acetic acid. W. D. H.

Levulose in Diabetes. By J. B. HAYCRAFT (*Zeit. physiol. Chem.*, **19**, 137—141).—Patients with chronic diabetes can burn off 50 grams of levulose per diem. In some acute cases, a part of the levulose given is burnt off, a part is changed into dextrose, and a third part passes as such into the urine.

Rabbits can make glycogen from levulose, the glycogen so formed accumulating in the liver (compare Voit, Abstr., 1892, 902).

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Yeasts. By P. HAUTEFEUILLE and A. PERREY (*Compt. rend.*, **118**, 589—591).—The yeasts that produce the fermentation of the wines of Côtes de Nuits and Beaune may, with scarcely any exceptions, be divided into three groups. The first group consists of apiculated yeasts, which produce fermentation at the outset, and in some cases complete it. The second group consists of ellipsoidal yeasts more active than the first group. They complete the fermentation, and in the later stages completely displace the apiculated yeasts, probably because the latter lose their fecundity after a certain number of generations.

The third group consists of ellipsoidal yeasts, which in a neutral or slightly acid must behave rather after the manner of high yeasts, and acquire a rose or wine-red coloration. They are generally present, but seem to have little activity, although in one case they

produced fermentation without the help of other yeasts; they show marked power of sporulation during their most active period, and even in a medium very favourable to nutrition, the sporulation takes place in the same manner as in the case of apiculated yeasts.

C. H. B.

Proteolytic Ferments in Seedlings. By R. Neumeister (*Zeit. Biol.*, **30**, 447—463).—Gorup-Besanez was the first to state that proteolytic and other ferments may be obtained from growing plants. This observation has been confirmed by some and contradicted by others. The cause of this discrepancy is to be found in the fact that different plants have been used by different observers, and that the methods employed are not calculated to settle the question definitely. The mere occurrence of albumoses and peptones in artificial digestive mixtures have in some instances been due to the hydrochloric acid used, and not to any ferment.

In the present experiments, advantage was taken of the circumstance that fibrin possesses the power of absorbing ferments from their solutions. Aqueous extracts of the seedlings were made; these were acid, and fresh fibrin was soaked in them; the fibrin was then removed, and placed in acid and alkaline mixtures, and the results observed, control experiments with acid and alkali alone being also performed.

Certain seedlings (barley, poppy, maize, wheat, rape) contain ferment which dissolves proteïd. It is not formed in the earliest stages, but increases as the plant grows, and is very abundant when the latter has reached the height of 15—20 centimetres. This ferment works, like pepsin, only in acid liquids, but hydrochloric acid destroys it; a vegetable acid like oxalic acid is necessary. It was not found in lupins, vetches, peas, rye, or oats.

The plants during growth yield peptone, formed from pre-existing proteïd, and there can be little doubt that the ferment described plays a part in its production, and that the peptone assists in the nutrition of the seedling.   W. D. H.

Presence of Saponins in Plants, and their Determination. By T. F. Hanausek (*Ann. Agron.*, **20**, 62—63; from *Chem. Zeit.*, **16**, Nos. 71, 72).—Authorities are not agreed as to the poisonous properties of corncockle seeds (*Agrostemma githago*). Recently, C. Kornauth and A. Arche have proved that pigs may be fattened on these seeds, which have for them the same nutritive value as barley. Other observers consider the seeds injurious, and maintain that where no harm occurs, it is because the saponins are in great part decomposed by the digestive juices.

The most important saponins, those characterised by Kobert, may be sought by the following microchemical reactions. Rosoll employed concentrated sulphuric acid. The root of saponaria and the bark of *Quillaja*, when treated with this reagent, show the contents of certain parenchyma tissue to be coloured yellow, red, and violet successively, but this reaction is also observed by concurrent action of the sulphuric acid on albumin, sugar, piperine, &c. A better plan is to use a mixture of equal parts sulphuric acid and alcohol.

Sometimes heat is necessary to produce the three colorations; a solution of ferric chloride thus produces a brown or blue-brown precipitate. The richer the drug in saprotoxins, the more does the blue colour predominate. This method has been tried with success on corncockle seeds, *Dianthus* seeds, fruits of *Sapindus, Saponaria,* and *Esculentus,* roots of Saponaria, *Senega, Polygala major,* and *Amara,* and bark of *Quillaja.* In *Polygala* root the saponins are contained in the sub-peridermic cellular layers. In seeds of *Agrostemma,* and *Dianthus,* the embryo alone contains saponinis. J. M. H. M.

Pentosans in Plants. By G. DE CHALMOT (*Amer. Chem. J.,* **16,** 218—229).—The author has made a number of determinations of pentosans in parts of plants of different ages and developments. The determinations were made by a slight modification of the method described by Flint and Tollens (Abstr., 1893, ii, 52), the mixed pentosans being estimated as equivalent to twice the furfuraldehyde found. A large number of determinations were also made in various woods, and in the different aged rings of the same pieces of wood. The results show that the quantity of pentosans increases during the development of the plants. Thus the young leaves of the red oak contained 5·29 per cent. of pentosans, the fully developed leaves of the same plant 9·77; axil parts of corn cobs, of which the seed was in the earliest stage of development, contained 29·3 per cent. pentosans, similar ripe cobs from the same set of plants, 33·3 per cent.; and similar results were obtained in other cases. The determinations in woods showed that the quantity of pentosans is increased during the formation of wood, but does not alter thereafter. The author has not been able to trace any relation between the percentage of pentosans in wood, and the hardness, toughness, or durability of the latter. The wood of dicotyledonæ is, however, much richer in pentosans than that of coniferæ, the former containing from 17 to 25 per cent. of pentosans, the latter only about 10 per cent. or less. The author considers that the pentosans are not waste products, but accumulate during the whole life of the plant, and probably act, in part at least, as reserve substances. They also seem to be of importance in the formation of wood, being specially developed at this stage.

L. T. T.

Occurrence of Trigonelline in Peas and Hemp-seed. By E. SCHULZE and S. FRANKFURT (*Ber.,* **27,** 769—770).—The undetermined base found in peas (Abstr., 1891, 490) has now been identified with the trigonelline obtained by Jahns (Abstr., 1886, 85) from *Trigonella* seed, and shown by him (Abstr., 1888, 166) to be identical with Hantzsh's synthetically prepared methylbetaine of nicotinic acid (Abstr., 1886, 369). It occurs, in small quantity only, both in green and dried peas (*Pisum sativum*), and in the seeds of hemp (*Cannabis sativa*). C. F. B.

Drainage Waters from Arable Soils. By P. P. DEHÉRAIN (*Ann. Agron.,* **20,** 21—42).—The present paper records the results

obtained in 1893 with the sunk water-tight cases filled with natural soil and subsoil, as described in a former paper (Abstr., 1893, ii, 338).

The rainfall from November 12, 1892 to March 2, 1893, the period to which the present record refers, amounted to 143·4 mm., and the drainage water from the case under bare fallow measured 65·5 mm., or nearly half the rainfall. This drainage water was analysed on the following dates.

					Gram.		Kilos.
Dec.	8/92.	Nitric nitrogen per litre			0·183,	per hectare	31·067
.,	14/92.	,,	,,	,,	0·157	,,	21·195
Jan.	5/93.	,,	,,	,,	0·011	,,	0·960
,,	20/93.	,,	,,	,,	0·009	,,	0·945
Feb.	8/93.	,,	,,	,,	0·078	.,	7·020
Mar.	2/93.	,,	,,	,,	0·116	,,	20·010

Thus, during January and February, nitrification was nearly at a standstill.

The author recognises that the loss of nitrates by drainage is in this first year of observation greatly exaggerated, the trituration and aëration of the soil, which occurred during the filling of the cases, having greatly promoted nitrification. The figures given by the various cases have, therefore, but a relative value. The general conclusions are :—

The losses by drainage are greater under bare fallow, the water percolating being both more abundant and richer in nitrates than in the case of soil under crop. In the latter case, the drains often do not run, and, when they do, the water is found nearly exhausted of nitrates by root absorption. The rotation most conducive to preservation of nitrate is that which keeps the land covered with green vegetation for the longest period. Thus potatoes or mangold grown for seed, allow more nitrate to be washed out in the autumn than mangolds grown for fodder. Wheat after mangolds, keeping the ground covered from April of one year to August of the next, allows little loss of nitrate ; but in the eight months fallow before mangold sowing much nitrate escapes, unless a winter fallow crop be taken during this interval. J. M. H. M.

Pentosans in Soils. By G. DE CHALMOT (*Amer. Chem. J.*, **16**, 229).—The author has estimated the pentosans in three soils, with the following results.

Description of soil.	Humus.	Pentosans.	Pentosans in 100 parts humus.
Wood soil	23·42 per cent.	0·75 per cent.	3·2
Garden soil	9·85 ,,	0·39 ,,	4·0
Poor sandy soil	2·68 ,,	0·04 ,,	1·5

L. T. T.

Farmyard Manure. By G. C. WATSON (*Bied. Centr.*, 1894, 239— 244).—In the winters 1891–2 and 1892–3, experiments were made to ascertain the relationship between the food consumed by domestic animals and the manure they produced. The animals employed for the purpose were sheep, cows, calves, pigs, and horses ; the con-

stituents of the manure were estimated, and appraised; it was found, generally, that the consumption of water was not dependant on the amount of dry food consumed, but on the nitrogen contained in the fodder.

The manurial values of various fodders were found to be as follows. Maize meal, 5·664 dollars per ton; ensiled green maize, 1·24; clover hay, 7·554; cotton-seed meal, 26·16; linseed meal, 19·36; flesh meal, 35·668; oats, 6·70; skim milk, 2·108; timothy grass hay, 4·60; wheat bran, 12·301; wheat straw, 2·127. The values of the nitrogen, phosphoric acid, and potash in each fodder are also given.

E. W. P.

Analytical Chemistry.

Phenomena of Oxidation and Chemical Properties of Gases.
By F. C. PHILLIPS (*Amer. Chem. J.*, **16**, 163—187).—A contribution
to the qualitative analysis of gases. The author has carried out a
very large number of experiments on the phenomena of the oxidation
of hydrogen and hydrocarbon gases by air in the presence of finely
divided metals and other oxidising materials. The finely divided
metal, coated on asbestos, was placed in a glass tube of $\frac{1}{8}$-inch bore,
and the mixture of air and gas passed through the tube while the
latter was gradually heated. The results obtained led to the follow-
ing conclusions: (1.) The temperature of oxidation is mainly de-
pendent on the solid substances with which the gas is in contact.
(2.) Two phases are often, but not always, to be observed in the
process of oxidation. As the temperature rises, a point is reached at
which a minute and scarcely recognisable trace of carbonic anhydride
appears; after this slow oxidation has continued for some time and
gradually increased during a rise in temperature of 20°, or 30°, or
even more, a sudden and intense reaction occurs; very often the
first slow oxidation is not observed. (3.) The oxidation of a hydro-
carbon by air, under conditions similar in all respects, does not
always occur at the same temperature, the variation in initial oxida-
tion temperature observed being sometimes considerable (in some of
the experiments exceeding 50°). A variation in the proportion of
inflammable gas and air does not seem materially to influence the
oxidation temperature. (4.) The paraffins are the most stable
towards air in presence of palladium; acetylene and carbonic oxide
stand next in order; the olefines are the most easily oxidised.
(5.) Of the members of the same homologous series, the lower are
the more stable towards oxidising influences. (6.) Hydrogen stands
alone among combustible gases in undergoing oxidation under the
influence of palladium coated asbestos in the cold. (7.) Oxidation
of gaseous hydrocarbons in excess of air involves the simultaneous
formation of carbonic anhydride and water; no selective oxidation
takes place, but oxidation is complete (that is, yields only carbonic

anhydride and water), even though a considerable portion of the hydrocarbon may escape unchanged. With insufficient air supply, the carbonic anhydride may be partly replaced by carbonic oxide. (8.) As regards oxidising power, the metals experimented with may be arranged in the following order, beginning with the most active : osmium, palladium, platinum and ruthenium, iridium, rhodium, gold. (9.) At a bright red heat, with excess of air, palladium asbestos causes oxidation of all hydrocarbons as efficiently as does ignited oxide of copper. (10.) The proportion of finely divided metal used upon the asbestos seems to be immaterial, palladium asbestos containing 2 per cent. of palladium, being nearly as efficient as that containing 30 per cent.

The author's results do *not* confirm Berliner's statements that (a) the catalytic action of each metal in the case of hydrogen begins at a fixed temperature and increases with rise of temperature ; (b) that the oxidation temperature for platinum foil is about 270°, for copper 280°, for zinc 350° ; and (c) that at constant temperature, the quantity of water formed is constant.

The following is a summary of the results obtained by the author with *palladium asbestos* and various gases, the figures given being the temperatures at which oxidation was observed to commence. Since, as mentioned above, this point varies considerably in different experiments carried out under apparently identical conditions, the lowest and highest initial oxidation temperatures observed are given :— Hydrogen, 20°, 55° ; methane, 404°, 414° ; ethane, 450° ; propane, 339°, 383° ; isobutane, 220°, 250° ; pentane, 170°, 210° ; heptane, 270°, 300° ; ethylene, 180°, 224° ; propylene, 170°, 200° ; trimethylene, 260°, 290° ; isobutylene, 155°, 185° ; acetylene, 339°, 359° ; benzene, 250°, 290° ; alcohol vapour, 150°, 240° ; carbon monoxide, 290°, 359° ; xylene gave very varying results. From these results, it is apparent that Hempel's method of determining hydrogen in the presence of other gases, by adding oxygen and passing the mixture over very slightly warmed platinised or palladinised asbestos, should give good results, but that the method cannot be safely extended to the selective oxidation of other gases.

To determine, if possible, whether the different initial oxidation temperatures observed in different experiments might be due to lack of uniformity of condition in the metal-coated asbestos, experiments were made on the initial temperatures at which oxidation of combustible gases was affected by copper oxide, lead chromate, silver oxide, silver permanganate, and silver dichromate. The same variations were however observed, the initial oxidation temperatures of ethylene by silver dichromate varying, in different experiments, from 260° to 320°. L. T. T.

Phenomena of Oxidation and Chemical Properties of Gases. By F. C. PHILLIPS (*Amer. Chem. J.*, **16**, 255—277; compare preceding abstract).—Among the solutions treated with hydrogen, the following suffered change:—*Palladium chloride;* slowly, but completely reduced, cold, or at 100°. *Platinum chloride;* very slow, but complete reduction, cold, or at 100°. *Ammoniacal silver nitrate;* slowly reduced to metal. *Potassium rutheniate;* slowly reduced to

metal. *Potassium permanganate;* slowly reduced, whether in neutral, acid, or alkaline solution. *Ferric chloride;* traces of reduction to ferrous chloride after several hours at 100°.

Russell (Trans., 1874, 3) states that silver nitrate solution is reduced by hydrogen; the author confirms Pellet (this Journal, 1874, 867).

The temperatures of reduction of metallic chlorides by hydrogen were found to be as follows:—Anhydrous ruthenium chloride, 190°. Gold chloride, obtained by evaporating a solution of gold in aqua regia to dryness, 150°. Anhydrous rhodium chloride, 200°. Platinum chloride, obtained by evaporating a solution of the metal in aqua regia to dryness, below 80° (with evolution of water as well as hydrogen chloride). Silver chloride, 270—280°. Silver bromide, 330—360°. Silver iodide, 350—370°. Palladium chloride was reduced in the cold.

To apply the reduction of palladium chloride as a test for hydrogen, the gas to be tested is dried by calcium chloride and phosphoric anhydride, conducted through a tube to the bottom of a dry test tube containing 0·2 gram of palladium chloride, and then into silver nitrate solution. The test tube should be kept cold if oxygen or hydrocarbon be present; otherwise it should be heated at 40° or 50°. The precipitation of the silver as chloride will detect 0·05 per cent. of hydrogen in absence of oxygen; in testing for such small quantities, oxygen should be removed by contact with ferrous hydroxide.

Silver oxide is reduced by hydrogen at 100°; iodic acid is not reduced by hydrogen at 250°.

Methane was found to have very little reducing action; potassium rutheniate was slowly reduced to metal. Chlorine attacks methane only at temperatures above 100°; a mixture of methane and chlorine exposed over water to sunlight underwent no contraction in volume nor change of colour. Methane reduces silver chloride at 414°, and silver bromide at 439°; silver iodide volatilises without reduction.

Ethane and heptane are as stable as methane; propane and isobutane are somewhat more easily oxidised.

The following solutions suffered change when treated with ethylene:—*Palladium chloride;* quickly reduced; no carbonic anhydride formed; aldehyde produced. *Gold chloride;* very slow reduction; no carbonic anhydride. *Ruthenium chloride;* bleached after prolonged contact; no metal reduced. *Potassium permanganate;* rapidly reduced. *Osmic acid;* quickly reduced to metal. *Potassium rutheniate;* quickly reduced to metal. *Bromine water;* rapid but incomplete absorption. Ethylene liberates iodine from iodic acid at about 270°.

Propylene is slightly more stable than ethylene, especially towards gold chloride and potassium rutheniate solutions.

Isobutylene behaves like ethylene and propylene, but from mercurous nitrate precipitates a grey powder, consisting of (or changing into) mercury. It bleaches iodine in potassium iodide, and cerium dioxide in sulphuric acid; neither reaction is shown by ethylene or propylene.

Isobutylene, prepared from isobutylic alcohol, causes a white precipitate in ammoniacal silver nitrate solution; that from isobutylic iodide and potash does not.

Trimethylene gives reactions similar to those of the true olefines, but is decidedly more stable towards many reagents; thus, it does not reduce osmic acid, potassium permanganate, or gold chloride.

The most important reactions for distinguishing between olefines and carbon monoxide are the following :—(1.) The action of palladium chloride solution, which is reduced by carbonic oxide with formation of carbonic anhydride ; the latter is not formed in the case of the olefines. (2.) Ammoniacal silver nitrate is not altered by olefines containing not more than 4 carbon atoms, but is reduced to silver and ammonium nitrite by carbonic oxide. (3.) Platinum chloride yields carbonic anhydride, but is not immediately reduced to metal by carbonic oxide. Ethylene produces no change. (4.) Rhodium chloride is slowly reduced by carbonic oxide, but is not altered by ethylene.

The author has failed to confirm Odling's statement that methane and carbonic oxide react at a high temperature to form water and acetylene.   A. G. B.

Estimation of Water in Hygroscopic Substances. By P. JANNASCH and J. LOCKE (*Zeit. anorg. Chem.*, **6**, 174—175).—A ∪-tube of hard glass has one limb wide, the bend enlarged to a bulb, and the other limb narrower, and bent at right angles a little above the first bend ; the laterally projecting end thus formed is ground into the end of a tube which contains dry lead oxide and is connected at its other end with a calcium chloride tube. The substance is pressed between filter-paper, and placed in the ∪-tube; dry air is then aspirated over it until its weight is constant, as determined by weighing the tube every five minutes, the ends being plugged during the weighing. Some dried lead oxide is then shaken down and mixed with the substance, and the mixture heated with a small flame, waved to and fro (so that the glass should not be attacked), whilst the water evolved is aspirated by a current of dry air into the calcium chloride tube, and there absorbed, and weighed. The method allows of the estimation of water in such substances as calcium and magnesium chlorides.   C. F. B.

New Mode of Performing Schlöesing's Nitric acid Estimation. By L. L. DE KONINCK (*Zeit. anal. Chem.*, **33**, 200—205).— The decomposition is effected in a fractionating flask, whose side tube is bent upwards and connected with a small funnel by caoutchouc tubing, which is compressed by a screw clamp. The gas evolution tube, which is of small bore, is fitted to the neck of the flask by a rubber stopper. It is bent downwards at an acute angle, and is so long that its lower end is 75—80 cm. below the bend. At its lower end, it is formed into a ⊢ piece, whose vertical tube, 6—7 cm. long and 7—9 mm. diameter, carries the graduated cylinder by means of a cork ring with radial notches on its upper surface. It rests on the bottom of a crystallising pan, containing as much mercury as will just close the end of the long tube, and the whole is plunged into a large vessel full of water. To make a determination, 40 c.c. of ferrous chloride (200 grams of iron to the litre), and 40 c.c. of hydrochloric

acid (1·1 sp. gr.) are placed in the flask, and the side tube is filled with acid up to the funnel. The liquid is then boiled until all air is expelled (the graduated cylinder being removed) ; the nitrate solution is placed in the funnel, and the lamp removed ; the mercury rises in the tube, but can never reach the top. The nitrate is rinsed into the flask with hydrochloric acid without admitting air, and the nitric oxide is boiled out, leaving the apparatus ready for the next determination. It is well to adopt Grandeau's suggestion to compare the volume of gas obtained in an analysis with that yielded by a known amount of a nitrate under the conditions as to time. The ferrous chloride in the flask suffices for as many estimations as will afford 800—900 c.c. of nitric oxide, or even for more if it is reduced again by adding stannous chloride. It is, however, absolutely necessary to avoid an excess of stannous chloride, and especially to leave none in the funnel and side tube.   M. J. S.

Volumetric Estimation of Phosphoric acid. By A. F. HOLLE-MAN (*Zeit. anal. Chem.*, **33**, 185—186).—See Abstr., 1893, ii, 490. From phosphates of the form M'_2HPO_4, to which state acid solutions of phosphates may be brought by adding phenolphthaleïn and then an alkali until the change of colour just occurs, the phosphoric acid is completely precipitated by silver nitrate in presence of excess of sodium acetate. A known quantity of silver is added, and the excess is titrated by Volhard's method. A large excess is to be avoided, as the results are then less exact.   M. J. S.

Estimation of Graphite in Pig-Iron. By F. L. CROBAUGH (*J. Amer. Chem. Soc.*, **16**, 104—108).—The author finds that very satisfactory results may be obtained by dissolving the metal in nitric acid (sp. gr. 1·135) and collecting the insoluble graphite and silica on two filters folded together, the outer one of which serves as a counterpoise. After drying at 100° and weighing, the inner filter is burnt and the weight of the silica ascertained. The graphite is then found by difference.

The silica may also be removed by treatment with nitric and hydrofluoric acids. Traces of carbon compounds may be got rid of by digesting the precipitate with dilute ammonia, or with a mixture of alcohol and ether.   L. DE K.

Copper Analysis. By J. S. DE BENNEVILLE (*J. Amer. Chem. Soc.*, **16**, 66—67, and *Chem. News*, **69**, 139—141).—The author has devised a method by which the great mass of the predominant constituents of copper alloys or pig-copper will remain in solution and the minor elements be concentrated in a small bulk, and corresponding ease in manipulation be obtained.

10 grams of copper is dissolved in nitric acid, any great excess of acid removed by evaporation, and ammonia added until the copper precipitate has redissolved. An excess of barium hydroxide is then added and the liquid filtered in about half an hour. The precipitate is well washed with dilute ammonia to remove any adhering copper salt. It may consist of lead, bismuth, tin, iron, manganese, and antimony ; arsenic and phosphorus are not completely precipitated. After

adding potassium cyanide to the ammoniacal filtrate, any silver, zinc, and cadmium may be precipitated with hydrogen sulphide. The treatment of the two precipitates is left to the discretion of the operator. L. DE K.

Analysis of Pig-Copper, Brass, and Bronze. By J. S. DE BENNEVILLE (*J. Amer. Chem. Soc.*, **16**, 133—140).—The author has studied the behaviour of tin towards nitric acid, and found that when the metal is evaporated with nitric acid for some time, it is completely converted into metastannic acid, which is insoluble in nitric acid, ammonia, and ammonium nitrate. If, when analysing a tin-copper alloy, the evaporation is pushed beyond a certain point, the oxide gets more or less contaminated with copper, manganese, iron, &c., which cannot be removed by washing with acid. If the tin is in excess, any phosphorus will be completely retained by the metastannic acid; any arsenic will also, for the greater part, enter into combination. These compounds are not properly decomposed by digesting with solution of sodium sulphide, but require fusion. Antimony behaves very similarly to tin, but its oxide is somewhat more soluble, particularly in dilute nitric acid. It does not retain phosphorus to the same extent as tin.

As tin oxide obtained from a copper alloy must always be purified, and as the separation of a small quantity of antimony from a large amount of copper, by means of sodium sulphide is, in practice, far from successful, the author strongly advises the concentration of the impurities in a small bulk by his ammonia-baryta process (see preceding abstract). L. DE K.

Detection of Aluminium. By G. NEUMANN (*Monatsh.*, **15**, 53—54).—The presence of a minute quantity of aluminium in ordinary samples of potassium hydroxide and sodium hydroxide renders any method of detecting the metal, in which one of these reagents is employed, extremely unsatisfactory. The following is suggested as giving trustworthy results. The iron, chromium, and aluminium, precipitated as oxides by barium carbonate, are boiled with barium hydroxide solution, and the filtrate made slightly acid with hydrochloric acid and precipitated hot with sulphuric acid. The filtrate is concentrated and treated with ammonia, when the formation of a white zone shows the presence of aluminium. G. T. M.

Estimation of Nickel in Nickel Steel. By E. D. CAMPBELL (*J. Amer. Chem. Soc.*, **16**, 96—102, and *Chem. News*, **69**, 139—141). —The sample is dissolved in nitrohydrochloric acid, and the iron with traces of copper precipitated by means of sodium acetate and sodium phosphate. An aliquot part of the filtrate is precipitated, while boiling, with potassium hydroxide, the precipitate, which contains all the nickel, is well washed and dissolved in dilute hydrochloric acid, and the solution is then digested with granulated lead to remove the copper, and filtered. A solution of sodium phosphate and dilute ammonia is now added to precipitate the manganese and traces of lead, and the whole made up to a definite bulk; an aliquot part of the filtrate is

used for estimating the nickel, which may be done by titrating with potassium cyanide, using cupric ferrocyanide as indicator, or by electrolysis. The latter method is preferable when cobalt is suspected, as this will be deposited with the nickel. L. DE K.

Estimation of Nickel in Steel. By J. WESTESSON (*J. Amer. Chem. Soc.*, **16**, 110—112).—1 gram of the sample is dissolved in 20 c.c. of sulphuric acid (sp. gr. 1·16) and the solution kept boiling for some time; the iron is now oxidised with nitric acid, the excess of which is then expelled by evaporation. The residue is dissolved in hot water, and after the bulk of the acid has been neutralised with sodium carbonate, the iron is precipitated as usual with sodium acetate, but it must be twice redissolved and reprecipitated. The united filtrates are concentrated to 400 c.c., mixed with 10 c.c. of strong ammonia, and boiled for a few minutes, so as to completely separate the manganese. (If ammonia be added to the liquid when cold, the manganese will not separate out, and will interfere with the estimation of the nickel.)

The nickel is now obtained by electrolytic deposition.

L. DE K.

Estimation of Potassium Iodide and Sodium Acetate in the Presence of Complex Organic Mixtures. By J. H. STEBBINS (*J. Amer. Chem. Soc.*, **16**, 157—159).—The author recommends the following process for the estimation of potassium iodide and sodium acetate in samples of medicine :—10 c.c. of the sample is evaporated with 30 c.c. of 20 per cent. sulphuric acid in a large platinum dish, first on a steam bath, then on a sand bath, and finally charred; the carbon is then burnt off with the aid of ammonium nitrate. The ash which is left, consists of mixed potassium and sodium sulphates, from which the metals are calculated by the ordinary indirect analysis. The iodine is estimated by diluting 10 c.c. of the sample with water, filtering from any precipitate, and adding an acid solution of silver nitrate. L. DE K.

Detection of Salicylic acid in Food. By K. P. MC ELROY (*J. Amer. Chem. Soc.*, **16**, 198—203).—The author tests for salicylic acid in canned vegetables as follows :—The contents of the can are pulped in a mortar, water and a little phosphoric acid are added, the mixture strained through a bag, and the liquid subjected to distillation. The first fractions hardly give any reaction with ferric chloride, as the acid has a tendency to accumulate in the later portions of the distillate, and the greater part of it is left in the distilling flask. The test with ferric chloride is safer than the reaction with Millon's reagent, which sometimes leads to erroneous results.

Hoorn has found that the distillation test is useless for beers, as in the process of fermentation certain phenol-like substances are formed which interfere with the reaction; but the author remarks that the presence of such compounds would also interfere with the shaking out process. [Hoorn has stated that six beers all gave salicylic acid reaction when distilled with a little sulphuric acid; all were free from salicylic acid when treated by the shaking out process.—Ab-

stractor.] The author also uses a shaking out process :—The beer or wine is extracted with half its volume of ether, the latter evaporated to dryness and the residue taken up with warm water. The solution is then tested in the usual way with ferric chloride. Although this process extracts the full amount of salicylic acid, the reaction is often not quite so distinct as when the distillation process is used.

L. DE K.

Estimation of Fat in Cheese. By S. BONDZYŃSKI (*Zeit. anal. Chem.*, **33**, 186—189).—The author employs for cheese the method suggested by Schmid for milk (Abstr., 1888, 1347), warming the weighed quantity of finely powdered cheese with 20 c.c. of 19 per cent. hydrochloric acid, until the casein is dissolved and the fused fat floats on the surface. 30 c.c. of ether is added, when the fat readily dissolves, and, either by the use of the centrifugal machine or by repose at 40°, the two layers separate sharply. After reading the volume of the ethereal solution, for which purpose the operation is performed in a flask with a calibrated neck, in the middle of which a bulb is blown, 20 c.c. of it is withdrawn and evaporated in a tared conical flask. M. J. S.

Estimation of Indigotin in Indigo. By F. DONATH and R. STRASSER (*Zeit. angw. Chem.*, 1894, 11—13; 47—50).—After reviewing the chief methods in use for the estimation of indigotin, the authors finally recommend the following process :—1 gram of the powdered sample is mixed with four times its bulk of ignited pumice-stone and exhausted in a Soxhlet-Szombathy extraction apparatus, first with warm, dilute hydrochloric acid, and then with a mixture of four parts of alcohol and one part of ether, to remove indigo-gluten and indigo-red. The residue is then extracted with about 30 c.c. of strong sulphuric acid for about two hours at 80°, the apparatus being suspended inside an air-bath. The solution is diluted with water to 1 litre, and 100 c.c. is diluted with 400 c.c. of water and titrated with potassium permanganate which has been carefully checked with pure indigotin under exactly the same conditions. L. DE K.

Estimation of Crude Fibre. By V. STEIN (*Exper. Stat. Record*, **5**, 613—614; from *Ugeskr. f. Landmänd*, **39**, 706—707).—The method for estimating crude fibre in cereals is as follows. The finely ground sample is freed from carbohydrates by treatment with malt decoction and subsequent washing with water; it is then treated with cold aqueous soda (1 per cent.), after which it is washed and treated with 1 per cent. hydrochloric acid, when it is allowed to settle. The residue is washed, transferred to a weighed filter (free from ash), washed with alcohol and ether, dried, and weighed. Nitrogen and ash are determined, and the amounts deducted. The results obtained are higher than those furnished by the Weende method. Samples of barley were found to contain 9·26 to 14·08 per cent. of crude fibre.

N. H. M.

General and Physical Chemistry.

Refraction Constants of Carbonyl Compounds. By R. NASINI and F. ANDERLINI (*Gazzetta*, **24**, i, 157—169).—The exceptionally high molecular refraction of nickel tetracarbonyl was attributed by Mond and Nasini (Abstr., 1891, 1322) to the octavalency of the nickel in this compound. Gladstone, however, is of opinion that the very high molecular refraction of ferropentacarbonyl (Abstr., 1893, ii, 254) is due to the peculiar arrangement of the carbonyl groups, and not to the presence of decavalent iron. The authors have measured the refraction constants of several carbonyl compounds, in order to ascertain whether the presence of a number of carbonyl groups in a molecule causes an abnormal increase in the molecular refraction similar to that observed by Zecchini in the case of the phenylamines (this vol., ii, 2).

The measurements were made for the ray $H\alpha$, and the results are summarised in the following table.

Substance.	$P\dfrac{\mu_{H\alpha} - 1}{d}$.		$P\dfrac{\mu_{H\alpha}^2 - 1}{(\mu_{H\alpha}^2 + 2)d}$	
	Observed.	Calculated.	Observed.	Calculated.
Quinone	48·27	46·80	27 98	27·28
Diacetyl	34·38	34·60	20 88	20 84
Dipropionyl	49·79	49·80	29 96	29 96
Tetrachlorotetraketohexa-methylene	83·67	82·90	49·04	48·32
Dibromodichlorotetraketo-hexamethylene.........	95 57	93·8	55·23	54·18
Leuconic acid..............	67·46	66·00	39·78	38 60
Potassium croconate.......	86 48	—	48 91	—

The refraction constants of quinone, tetrachlorotetraketohexamethylene, $CCl_2{<}^{CO \cdot CO}_{CO \cdot CO}{>}CCl_2$, and dibromodichlorotetraketohexamethylene were measured in benzene solution; leuconic acid and potassium croconate were examined in aqueous solution.

Leuconic acid combines with 5 mols. of water of crystallisation or combination; in aqueous solution it seems to possess the constitution $C(OH)_2{<}^{C(OH)_2 \cdot C(OH)_2}_{C(OH)_2 \cdot C(OH)_2}$, since the molecular refractions calculated for this formula which are given in the above table agree closely with the observed values.

If the atomic refraction of potassium is taken as 8 1—the value deduced by Gladstone from the refraction of potassium salts—the

calculated molecular refraction of potassium croconate becomes 58·20 for the formula $P\dfrac{\mu - 1}{d}$; the atomic refraction of potassium must be taken as 22·5 for the simple formula and 12·40 for the μ^2 formula if the ordinary constant is assigned to the carbonyl groups. The authors attribute the abnormally high molecular refraction of this substance to the metal alone, since the measurements made on the other carbonyl compounds show that the presence of several carbonyl groups causes no abnormal increase in the molecular refraction. They do not deny that the anomalous results obtained with such compounds may be partly due to the measurements being sometimes made in solution, as supposed by Perkin (Trans., 1892, 800).

<div style="text-align: right">W. J. P.</div>

Refraction Constants of Furfurylic Alcohol and of Pyromucic acid and its Salts. By G. GENNARI (*Gazzetta*, **24**, i, 246—255; compare following abstract).—The author has determined the refraction constants of furfurylic alcohol and of pyromucic acid, (HPy), and several of its ethereal salts, for the lines H_α, H_β, H_γ, and D. The results for the ray H_α are summarised in the following table.

Substance.	Temp.	$P\dfrac{\mu_{H_\alpha} - 1}{d}$.	$P\dfrac{\mu_{H_\alpha}^2 - 1}{d(\mu_{H_\alpha}^2 + 2)}$.	Atomic refraction of the furfurylic oxygen.	
				From μ.	From μ^2.
Furfurylic alcohol.	22·7°	42·2	24·75	2·6	0·97
HPy in H_2O......	22·6	44·02	26·18	2·82	2·14
„ EtOH....	23·5	45·1	27·1	3·9	2·14
MePy	21·4	51·57	30·50	3·77	2·74
EtPy	20·8	59·4	35·29	3·14	1·90
PrPy	25·9	67·3	39·95	3·3	2·13
$CHMe_2·Py$	23·7	67·0	39·90	3·09	2·23
$CMe_3·Py$	27·5	—	44·6	3·44	2·18

The constants for pyromucic acid were determined in a 3·264 per cent. aqueous solution and in alcoholic solutions containing 19·522 and 25·06 per cent.; the values of the latter solution are considerably higher than those for the other two, which are given in the table. The other substances were examined in the pure state.

<div style="text-align: right">W. J. P.</div>

Refraction Constants of Oxygen, Sulphur, and Nitrogen in Heterocyclic Nuclei. By R. NASINI and G. CARRARA (*Gazzetta*, **24**, i, 256—290).—The authors have determined the refraction constants of a number of substances containing oxygen, sulphur, or nitrogen in a closed chain for the rays H_α, H_β, H_γ and D. The results for the line H_α are tabulated below.

Substance.	$t.°$	$P\dfrac{\mu-1}{d}.$	$P\dfrac{\mu^2-1}{(\mu^2+2)d}.$	Atomic refraction of the S, N, or O in the nucleus.	
				For μ.	For μ^2.
Furfuran	21·6	30·46	18·42	0·46	0·78
1 : 4-dimethylfurfuran....	17·7	46·75	28·01	1·55	1·25
Thiophen	25·1	41·40	24·18	11·40	6·54
1 : 4-dimethylthiophen ...	19·0	57·87	34·02	12·67	7·26
Pyrroline	21·0	35·09	21·39	3·79	1·86
1 : 4-dimethylpyrroline ...	19·8	50·83	29·90	4·33	2·10
Pyridine................	12·4	40·72	23·87	4·42	2·73
Picoline	—	48·78	28·54	4·88	2·82
Quinoline	20·0	73·03	41·38	9·33	4·66
Isoquinoline............	21·4	72·30	40·01	8·59	4·29
Piperidine	23·8	44·46	26·55	5·16	2·71
Coniine.................	23·0	67·86	40·51	5·76	2·99
2-Methylpyrazole	13·7	39·32	23·20	4·56	2·63
3 : 5-Dimethylpyrazole ..	25·7	48·02	28·39	5·11	2·94
1-Phenyl-3:4-dimethylpyrazole	19·4	92·12	53·09	5·96	3·10
1 : 4 : 5-Phenylmethylethylpyrazole	22·0	101·63	58·53	6·91	3·54
1 : 4 : 3 : 5-Phenyldimethylethylpyrazole	19·8	107·59	62·17	6·09	3·08

The values given for thiophen are calculated from Nasini and Scala's numbers (Abstr., 1887, 754). 3 : 5-Dimethylpyrazole was examined in an 11·209 per cent. benzene solution, but all the other compounds were examined in the pure state. The authors give a full discussion of the results, and consider that they support the conclusion that heterocyclic nuclei, like furfuran, pyrazole, &c., have a centric constitution similar to that which is by some attributed to benzene. W. J. P.

Constitution of Benzene. Refraction Constants and Molecular Volumes of Benzene Derivatives. By J. W. Brühl (*J. pr. Chem.*, [2], **49**, 201—294; *Ber.*, **27**, 1065—1083). See this vol., i, 366.

Spectra of Tin, Lead, Arsenic, Antimony, and Bismuth. By H. Kayser and C. Runge (*Ann. Phys. Chem.*, [2], **52**, 93—118).— Of the elements of the fourth and fifth groups of the periodic system, only a few can be utilised for spectroscopic measurements. Germanium and the rare earths cannot be obtained in sufficient quantity or purity, carbon and silicon give only very few lines, and nitrogen and phosphorous no lines at all. The authors have therefore confined their observations to tin and lead in the fourth, and arsenic, antimony, and bismuth in the fifth group, the method employed being that described in former communications (Abstr., 1893, ii, 313).

Regularities similar to those observed in the spectra of other metals belonging to the same groups in the periodic system were not discovered, as the lines do not arrange themselves in series. There are, however, in all these spectra groups of lines which are repeated at least three times over, and between which there are constant differences in the vibration periods.   H. C.

Absorption Spectra of Cupric Bromide. By P. SABATIER (*Compt. rend.*, **118**, 1042—1045).—The author has examined the absorption spectra of solutions of copper bromide of different concentrations. Very concentrated solutions are extremely opaque and only admit of examination in layers of less than 1 mm. in thickness. The absorption spectra of such solutions is similar to that of solutions of the salt in alcohol. The absorption for these solutions is greatest in the green, and transmission is at a maximum in the red. As the solutions are diluted, the absorption in the green decreases and that in the red increases, until with very dilute solutions, absorption is at a maximum in the red and very slight in the green.   H. C.

Variation of Rotatory Power under the Influence of Temperature. By A. LE BEL (*Compt. rend.*, **118**, 916—918).—In order to avoid the probable presence of amylic alcohol, the author has prepared amylic isobutylic ether by the action of amylic chloride on sodium isobutoxide. The product thus obtained gives the following rotations in a column 200 mm. long.

$t°$	$65°$	$15°$	$-42°$
Rotation	$+1° 28'$	$+1° 13'$	$+34'$

Methylic lactate shows similar variations.

$t°$	$100°$	$15°$	$-23°$
Rotation	$-4° 27'$	$-4° 2'$	$-2° 41'$

All the compounds actually known to have variable rotatory power are compounds in which the asymmetrical carbon atom is united only with a single radicle containing an atom of oxygen united with another radicle. When, on the other hand, the asymmetrical carbon is united with two radicles of similar constitution, the variations of the rotatory power become almost *nil*. The rotatory power of methylic tartrate, for example, varies considerably with the temperature, whereas the rotatory power of methylic valeryltartrate is practically constant, and the tetra-substituted ethereal salts of tartaric acid show no variations between 10° and 100°.

With a view to ascertain whether these variations are due to polymerisation or to changes in the internal structure of the molecules, Ramsay has determined the molecular weights of some of the compounds. Propyl glycol has a quadruple molecular weight at the ordinary temperature and a double molecular weight above 100°, but the rotatory power does not vary. Ethylic tartrate has a simple molecule at about 100°, but probably polymerises at low temperatures, when the rotatory power is much lower. Amylic isobutylic ether, however, has a simple molecule between −23° and +125°, and hence

the variations in rotatory power observed by the author and by Colson must be due to internal changes.

The facts can only be reasonably explained by assuming that the univalent unions become immobile at low temperatures, the molecule undergoing a kind of internal congelation. C. H. B.

The Voltaic Chain. By H. M. GOODWIN (*Zeit. physikal. Chem.*, **13**, 577—656).—The author describes experiments made to test the validity of the law, that the potential difference between a metal and a solution depends on two constants—(1) a constant for the metal, (2) the cathion concentration of the solution. Two cases are considered: when the solution is (i) that of a salt of the electrode, (ii) that of a sparingly soluble salt of the electrode in the presence of a soluble salt containing the same anion. The cause of the difference of potential is considered to be the emanation of ions from the metal into the solution until the ion pressure (p), together with the electrostatic attraction of the metal for the ions —$f(s)$—, is equal to a value P, constant for the metal. If the pressure p were originally greater than P, then the metallic ions would be deposited upon the metal until $p - f(s) = P$; $f(s)$ being in this case, of course, a repulsive force. Starting from this view, and equating the change of volume energy to that of electric energy, a value is obtained for the potential difference. As in the experiments, the E.M.F. of a cell with the same electrodes in different solutions was employed, the final equation is independent of P; E.M.F. $= \dfrac{RT}{n_\epsilon \epsilon_0} \log_\epsilon \dfrac{p_1}{p_2}$, where n_ϵ is valency of metal, p_1 and p_2 the ion pressure, and ϵ_0 the electric equivalent 96,450 coulombs. A number of experiments follow with a chain of the nature of Case I—thallium, thallium chloride, and potassium nitrate, thallium chloride and potassium chloride, thallium—and the observed values agree well with these calculated by the formula developed, as is also the case when the salts of other metals are substituted for those of potassium. For the consideration of Case II, two chains of zinc, zincic chloride, mercurous chloride, mercury, with varying concentrations are opposed, and the observed and calculated values compared and found concordant. A number of changes are made which should theoretically have no effect on the E.M.F., such as substitution of bromides for chlorides, of silver and silver chloride for mercury and mercurous chloride, &c., and the results found as predicted. In the third portion of the communication, the author points out a method for the determination of the solubility of salts by the measurement of the E.M.F., and the results thus obtained are compared with those deduced by other methods. In the case of very insoluble salts, such as silver iodide, very different results are obtained by the different methods. The author considers the E.M.F. method the best when the solubility is below 0.1×10^{-5}, but for higher solubilities he regards the conductivity method as preferable. L. M. J.

Copper Electrolysis in a Vacuum. By W. GANNON (*Proc. Roy. Soc.*, **55**, 66—83).—It is known that copper sulphate in solution does not conform rigorously to the simple form in which Faraday's

law of electrolysis is generally expressed, and it has been shown by Gray that the copper deposit is heavier the higher the current density and the lower the temperature, an explanation of this being given in the fact that copper dissolves to a very appreciable, although variable, amount in solutions of copper sulphate. According to Schuster, it is probably the oxygen of the air present in the solution that causes this chemical corrosion, and hence it was of interest to examine if any difference could be found between the weights of the deposits of two copper voltameters, one of which would be placed in a vacuum.

The author shows that with two copper voltameters containing freshly made neutral solution of copper sulphate, one of which is under reduced pressure, the other conditions being comparable, the copper deposit in the partial vacuum is higher than the deposit under the atmospheric pressure, but the percentage difference is not constant. If a little free sulphuric acid be added to the air solution, the percentage difference is more constant and higher than before. The addition of acid to both voltameters causes the percentage difference to be constant within experimental errors. Under this last condition, for current densities above 0·01 ampère per sq. cm. of active cathode, there is no practical difference between the two deposits, but for densities below 0·01 ampère per sq. cm., the vacuum deposit is very appreciably higher than the air deposit. A curve drawn representing the deposits obtained in a vacuum at different current densities is more regular than the air curves, and for densities below 0·01 ampère per sq. cm. is approximately a straight line.   H. C.

Specific Heats and Latent Heats of Change of State of Solid Silver and Copper Sulphides and Selenides. By M. BELJATI and S. LUSSANA (*Zeit. Kryst. Min.*, **23**, 167—170; from *Atti Istit. Venet* (6), **7**, 1051).—The remarkable anomalies in the electrical resistances of silver and copper selenides at different temperatures observed by the authors (*Atti Istit. Venet.* (6), **6**, 189) have led them to investigate the rate of heating and cooling of the sulphides and selenides having the composition Cu_2S, Ag_2S, Cu_2Se and Ag_2Se; it was thereby ascertained that these substances change into physically isomeric forms at definite temperatures. The change is, of course, accompanied by the development or absorption of heat, and the different physical modifications have different specific heats. The following table gives the heat of conversion, λ, in small, mean calories, and the two specific heats, γ just below the temperature of change t, and γ_t just above that temperature.

Substance.	t.	λ.	γ.	γ_1.
Cu_2Se...	110°	5·405	0·09805	0·08505
Ag_2Se	133	5·641	0·06836	0·06843
Cu_2S	103	5·630	0·13465	0·15330
Ag_2S	175	3·843	0·08914	0·08364

The anomalous changes in the electrical resistances of these sub-

stances with temperature are thus explained by their peculiar behaviour towards heat; it is noteworthy that the electrical resistance and the specific heat of silver sulphide have constant values from 79° to 175°, the temperature at which change of state occurs. W. J. P.

Fusibility of Mixtures of Salts. By H. LE CHATELIER (*Compt. rend.*, 118, 800—804).—Mixtures of salts capable of forming double salts correspond with aqueous solutions of salts which form hydrates, and the author has previously shown that, in the case of the latter, each different compound, or each different state of the same compound, has a distinct curve of solubility. It follows that salts capable of forming a single definite compound will have a curve of fusibility consisting of three parts, one corresponding to the crystallisation of one of the salts, the second to the crystallisation of the other simple salt, and the third to the crystallisation of the double salt. The curves of the two single salts have the same form as if the double salt did not exist. The curve of the latter necessarily has a different form; its highest temperature of crystallisation is that which corresponds with its simple fusion, but this diminishes gradually when increasing quantities of one or other of the constituent salts are added, and tends, in the two cases, to approach absolute zero when the proportion of one or other of the single salts tends to become *nil*. The three curves, when taken in pairs, show a certain number of points of intersection which limit the available parts of the curves. The portions corresponding with a state of stable equilibrium are necessarily those which, for a given mixture, correspond with the highest temperature of crystallisation, in those cases, at least, where crystallisation is accompanied by a development of heat. The crystallisation of the double salt may take place between limits more or less extended, according to the relative position of the three curves, or even may not take place at all if its curve is entirely below those of the two simple salts. When part of the curve of the double salt is above that of the single salts, sometimes its summit (which corresponds with the melting point of the isolated double salt) will be on the stable part of the curve, and in this case the double salt can be fused without decomposing; if, however, the summit is outside the stable part of the curve, the fusion of the double salt is accompanied by precipitation of one of the constituents. The first case has been observed with some aqueous solutions, but is quite exceptional; the second case is that of the majority of saline hydrates which can be formed in aqueous solutions.

Curves are given for lithium potassium carbonate and for sodium phosphoborate respectively. The former contains equal equivalents of its constituents, is perfectly crystalline, and shows strong double refraction; the latter has no action on polarised light. The mixture of lithium and potassium carbonates shows supersaturation, which allows the curve of the double salt to be prolonged beyond that of potassium carbonate, a result analogous to that which would be obtained if a solution of sodium chloride could be cooled below the freezing point of its cryohydrate or eutectic mixture without solidification taking place. C. H. B.

An Improved Specific Gravity Bottle. By H. Louis (*J. Soc. Chem. Ind.*, 1894, 322—323).—The new bottle differs from the ordinary type only in that the stopper is longer than usual, and is graduated, whilst a light glass cap is ground to fit accurately over the neck of the bottle, and thus to prevent the loss by evaporation that otherwise occurs during weighing, &c. It is filled in the usual way; the neck and stopper are then rapidly wiped dry, the cap is put on, and the body of the bottle dried. When weighing the bottle, any variation in the height of the column of liquid in the capillary tube must be read off on the graduations, which may be to any convenient scale; the author's graduations are $\frac{1}{20}$ in. apart, corresponding with $\frac{1}{100}$ grain of water. It is an easy matter to calibrate the tube and to make the necessary corrections. The capped bottle can be left for a long time without diminishing in weight through evaporation taking place.   L. DE K.

Rate of Diffusion of some Electrolytes in Alcohol. By W. KAWALKI (*Ann. Phys. Chem.*, [2], **52**, 166—190).—In this, the first portion of the author's communication, the method of experimenting, which is similar to that of Scheffer (Abstr., 1888, 1144), is described. The application of Stefan's tables for calculating the diffusion coefficient is considered, and a modification given, which is better suited to the author's arrangement.   H. C.

Densities of Solutions of Soda and Potash. By S. U. PICKERING (*Phil. Mag.*, [5], **37**, 359—375).—The only existing data as to the densities of these solutions are very inaccurate and antiquated. In the present series, the mean experimental error is 0·0000063. The results with soda, which extend from 50 per cent. downwards and apply to a temperature of 15°, when plotted form a figure which is eminently complex, and shows eight breaks, several of which are very well marked. Of these, six occur at points corresponding with the hydrates already isolated by the author (Trans., 1893, 890); the other two, which occur in weak solutions, correspond with the only two breaks found in the freezing point figure. A drawing, showing the above-mentioned breaks, attributes to the points an apparent error, agreeing almost absolutely with the known experimental error, whereas a drawing of a similar degree of complexity, placing the breaks elsewhere, gives an apparent error 6·6 times greater than the experimental error, and drawings obliterating every alternate break give errors 18 to 33 times greater. The results with potash form a simpler figure, and indicate somewhat uncertainly the existence of four breaks, one of which corresponds with the recently isolated tetrahydrate.   S. U. P.

Solubility of Mercuric Haloïds in Carbon Bisulphide. By H. ARCTOWSKI (*Zeit. anorg. Chem.*, **6**, 260—267).—The solubility of mercuric chloride, bromide, and iodide in carbon bisulphide has been determined between −10° and +30°, and the results plotted against the temperature. The curve in each case consists of two straight lines, and indicates that the solubility increases with the temperature

at a constant rate until a certain point is reached, after which it increases at a greater, but still constant, rate. The solubility of the iodide is greater than that of the bromide, and increases with the temperature at a greater rate; the same is true of the bromide as compared with the chloride. The points of change of curvature of the three curves lie approximately on a straight line; the lower parts of the three curves intersect approximately in a point on the axis of temperatures, and they diverge almost at equal angles; and the straight line passing through the two points, given by special determinations of the solubility of the iodide at $-21°$ and at $-76°$, intersects the axis of temperatures at a point almost coincident with the freezing point of the solvent.

Carbon bisulphide has no tendency to form molecular compounds with mercuric haloids, and it is thus impossible to account for the breaks of continuity in the above-mentioned curves in the same way as is done when the breaks in the curve of solubility of sulphuric acid in water are assumed to be due to the existence of definite hydrates, some of which it is possible to isolate. The author seems, indeed, to regard these hydrates as effects, rather than causes, of the phenomenon of solution. He looks on a solution as an ill-defined molecular compound between solvent and dissolved substance, and supposes that, when one thing does not dissolve in another, it is because the two substances are incapable of forming such compounds. The language of the paper is somewhat obscure on these points, probably due to its being a translation.   C. F. B.

Velocity of Hydrolysis of Methylic Acetate by Water. By J. J. VAN LAAR (*Zeit. physikal. Chem.*, **13**, 736—756).—The value for the electrolytic dissociation of water, obtained by Wijs (Abstr., 1893, ii, 364) from experiments on the hydrolysis of methylic acetate is considerably less than that obtained by Bredig, Walker, and Ostwald by other methods. The author first deduces an expression for the quantity of ethereal salt hydrolysed as a function of the time, and also for the point of least velocity, and compares the results with Wijs' experiments, and is of the opinion that the value obtained by Wijs, 1.2×10^{-7}, must be regarded as the most probable value and be accepted until more accurate determinations are made.

L. M. J.

Velocity of Reaction between Ethylic Iodide and Sulphide. By G. CARRARA (*Gazzetta*, **24**, i, 170—179).—The reaction between ethylic iodide and ethylic sulphide is represented by the equation $Et_2S + EtI = SEt_3I$, triethylsulphine iodide being formed. The reaction is consequently of the second order, and should be represented by the equation $\dfrac{dx}{dt} = C(A - x)(B - x)$, where A and B are the molecular quantities of the interacting substances, x the amount of substance transformed during the time t, and C a constant. If the interacting materials are employed in equivalent proportion, A and B become equal, and, on integrating, it is seen that $\dfrac{x}{t(A - x)}$ is constant.

The weighed mixture of ethylic sulphide and iodide in molecular proportion was placed in a closed tube, heated to the desired temperature for a known time, and then plunged into ice; the contents of the tube were filtered after adding ether, and the triethylsulphine iodide titrated in aqueous solution against standard silver nitrate. The constant given above was thus found to be 0·00013 at 41°, 0·00034 at 66°, and 0·00014 at 80°, the individual numbers for the two lower temperatures agreeing fairly well. The results obtained at 80° are not altogether satisfactory, owing to the partial decomposition of the triethylsulphine iodide at that temperature; at 100°, very little of the sulphine was obtained, only 0·65 per cent. of it remaining undecomposed after 990 minutes.

The presence of water considerably accelerates the action, and the above equation no longer holds, the system not being homogeneous. The author attributes this accelerating action to the greater stability possessed by the triethylsulphine iodide when partially dissociated in aqueous solution than when in the pure state.   W. J. P.

Effect of Neutral Solvents on the Velocity of Formation of Triethylsulphine Iodide. By G. CARRARA (*Gazzetta*, **24**, i, 180—189; compare preceding abstract).—The velocity of reaction between ethylic iodide and sulphide in solution changes as the solvent employed is changed. The following table shows the factors by which the velocity increases on the addition of various neutral organic solvents, the velocity coefficient 0·00034 at 66° (see preceding abstract) being taken as unity.

Solvent.	At 66°.	At 78°.	At 100°.
MeOH, 1 mol.	—	—	60·3
MeOH, 1 vol.	15·3	50·9	273·1
MeOH, 2 vols................	—	—	181·7
MeOH, 4 vols..	—	—	107·6
EtOH, 1 vol........	7·6	16·5	42·9
$CH_2Et\cdot OH$, 1 vol.	4·7	12·9	24·7
$CHMe_2\cdot OH$, 1 vol.......... ..	4·1	7·6	—
$COMe_2$, 1 vol.	—	—	0·44

It will be seen from the table that alcohols increase the speed of the reaction, whilst acetone decreases it; the action does not proceed in presence of benzene or ether. The author agrees with Menschutkin that the cause of the different effects of various solvents on the velocity of reaction is not a physical one, but must be sought in the chemical constitution of the solvents themselves.   W. J. P.

Atomic Weights. By J. THOMSEN (*Zeit. physikal. Chem.*, **13**, 726—736).—The paper contains recalculations of the atomic weights as obtained from Stas' experiments and referred to O = 16. Silver is first calculated from five independent methods, and the mean value $O_2/Ag = 0·444733$ obtained, whence Ag = 107·9299. From the value of silver, the numbers for chlorine, bromine, and iodine are

obtained, and from these, those for other elements, the results being contained in the accompanying table, together with Stas' own numbers and those recalculated by Van der Plaats.

	Stas.	Thomsen.	Van der Plaats.
Ag	107·930	107·9299	107·9244
Cl	35·457	35·4494	35·4565
Br.	79·952	79·9510	79·9548
I	126·850	126·8556	126·8494
S..........	32·074	32·0606	32·0590
Pb..	206·934	206·9042	206·9308
K	39·1425	39·1507	39·1403
Na..........	23·0455	23·0543	23·0443
Li	7·022	7·0307	7·0235
N	14·055	14·0396	14·0519

The author then points out that his numbers are preferable to those of Van der Plaats, inasmuch as they reproduce the original experimental numbers with a higher degree of accuracy, the average difference from the experimental ratios being only one-sixth of that obtained by the use of Van der Plaats' numbers, while further the differences are more uniformly distributed amongst the positive and negative signs. The value for hydrogen as calculated from the ratio NH_3/HCl (this vol., ii, 277) with the above values for nitrogen and chlorine becomes $H = 0·9992$. L. M. J.

Apparatus for Distillation in a Vacuum. By F. ANDERLINI (*Gazzetta*, **24**, i, 190—191).—A somewhat complicated glass apparatus for use in distillation under reduced pressure is described and figured ; it consists of a bell jar, into the neck of which is ground a stopper through which passes an adapter for taking the end of the condenser. The bell jar contains the vessels for collecting the distillate, and may be turned round in order to direct the separate fractions into the proper receptacles, the stopper remaining fixed.

The author employs Wurtz flasks having a small auxiliary bulb in the neck and a stem of some 50—60 cm. in length. Instead of filling the distilling flask with glass wool, as recommended by Angeli (this vol., ii, 39), the author prefers to stand a bundle of glass threads in the bulb, keeping them in place by a spiral of platinum wire contained in the neck of the flask. W. J. P.

Inorganic Chemistry.

Atmospheric Hydrogen Peroxide. By E. Schöne (*Ber.*, **27,** 1233—1235; compare this vol., ii, 88).—A reply to Ilosva's paper on this subject (this vol., ii, 277). Exception is taken to the statements that nitric peroxide is a constant constituent of air, and is the oxidising agent in it. The chief question at issue is one of fact, namely,

whether potassium iodide, starch, ferrous sulphate, and guiacum diastase solutions are characteristic reagents for hydrogen peroxide, and although Ilosva denies this, the author has recently furnished detailed experimental proof in support of his assertion (*Zeit. anal. Chem.*, 1894, 137). In addition to hydrogen peroxide, organic peroxides, such as percarbonic acid, are probably present in the atmosphere, they are formed by plants in the presence of sunlight (compare Bach, this vol., ii, 186). J. B. T.

Chlorides and Iodides of Nitrogen. By T. SELIVANOFF (*Ber.*, **27**, 1012—1019).—The chlorides and iodides of nitrogen are considered by the author to be the amido-derivatives of hypochlorous and hypoiodous acids. Iodide of nitrogen is most probably formed by the action of ammonia on hypoiodous acid, which, along with ammonium iodide, is the first product of the reaction between ammonia and iodine.

$$(\text{I.})\ NH_3 + H_2O + I_2 = NH_4I + HOI.$$
$$(\text{II.})\ (a)\ 2NH_3 + 3HOI = NH_3\!:\!NI_3 + 3H_2O.$$
$$(b)\ NH_3 + 2HOI = NHI_2 + 2H_2O.$$
$$(c)\ NH_3 + 3HOI = NI_3 + 3H_2O.$$
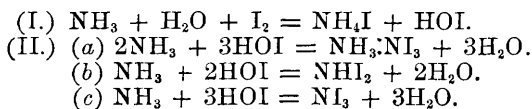
When a dilute solution of iodine is added to ammonia, the liquid remains clear and contains hypoiodous acid. When a further quantity of iodine is added, iodide of nitrogen is precipitated, and the clear liquid then contains less hypoiodous acid than before. On the other hand, iodide of nitrogen is soluble in a large amount of ammonia, yielding a solution which contains hypoiodous acid, so that the equations (a), (b), and (c) given above are reversible. It is to this formation of hypoiodous acid that many of the characteristic reactions of iodide of nitrogen must be referred, such as the liberation of oxygen from hydrogen peroxide, the formation of chloride of iodine by the action of hydrochloric acid, and the production of iodine derivatives from phenol. The accuracy of this view is further confirmed by the action of potassium iodide solution and of dilute acids on iodide of nitrogen.

Potassium iodide dissolves all the iodides of nitrogen more or less readily, and the solution formed contains ammonia, iodine, and caustic potash, the reaction being represented by the following equations :

$$NHI_2 + 2H_2O = NH_3 + 2HOI,$$
$$2HOI + 2KI = 2I_2 + 2KOH.$$
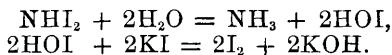
Dilute acids, on the other hand, convert iodide of nitrogen into iodine and iodic acid, both of which are formed from hypoiodous acid according to the equation

$$5HOI = 2I_2 + HIO_3 + 2H_2O.$$
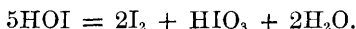
The change is usually accompanied by a certain amount of decomposition into iodine and nitrogen, but this can be wholly avoided if (1) a small amount of acid be employed, (2) sufficient water be present to dissolve the whole of the iodine formed, and (3) the iodide of nitrogen be in the form of a very fine powder.

In the light of the formation of the iodides of nitrogen by the

action of ammonia on hypoiodous acid, the author proposes the following names for the these substances : $NH_3 \cdot NI_3$, *sesqui-iodylamide;* NHI_2, *di-iodylamide;* NI_3, *tri-iodylamide.*

The chlorides of nitrogen are probably always formed in a similar manner to the iodides by the action of ammonia on hypochlorous acid, a reaction which has been used for their preparation. When chloride of nitrogen is treated with dilute sulphuric acid, it is partially dissolved, the solution giving the reactions of hypochlorous acid ; the accumulation of hypochlorous acid, however, prevents any further decomposition of the chloride, and the greater part of it therefore remains unchanged. When hydrochloric acid is employed, on the other hand, the hypochlorous acid is decomposed with formation of chlorine as fast as it is formed, and the entire amount of chloride of nitrogen is rapidly decomposed. In the same manner, chloride of nitrogen is completely decomposed by a solution of succinimide, which reacts with the hypochlorous acid to form chlorylsuccinimide (Abstr., 1893, i, 192).

Other interesting reactions of chloride of nitrogen are that solid iodine produces an explosion, whilst a dilute solution yields iodic acid, and that it undergoes an energetic reaction with potassium iodide, iodine being liberated.   A. H.

Preparation of Free Hydroxylamine. By J. W. BRÜHL *(Ber.,* **27**, 1347).—Polemical. A rejoinder to Lobry de Bruyn (this vol., ii, 278).

Phosphoric Anhydride. By H. BILTZ *(Ber.,* **27**, 1257—1264).— Ammonia reacts energetically with phosphoric anhydride at ordinary temperatures, forming a dark reddish-brown mass consisting chiefly of phosphamic acid. On treatment with water, hydrogen phosphide is evolved, and yellow phosphorus (0·05 per cent.) is formed, together with a reddish, flocculent substance (0·1—0·2 per cent.). This substance is not red phosphorus, as Schiff stated, but the suboxide, P_4O. By the action of potash, hydrogen phosphide is formed ; in presence of moisture, white vapours are evolved, and on warming with sulphuric acid, phosphoric acid and sulphurous anhydride are formed. Phosphorus suboxide is formed in small quantity by heating phosphoric anhydride at 250° either in a vacuum or in a current of air, carbonic anhydride, hydrogen, oxygen, or steam ; the maximum yield is 0·06 per cent. ; it is also formed in traces by dissolving the anhydride in water or soda. The formation of the suboxide is conditioned by a high temperature, and the presence of phosphorus oxide in the phosphoric anhydride, since it is not formed by the action on the latter of water in large excess, of ammonia at low temperatures, or in any circumstances from water or ammonia, and anhydride which has been purified by sublimation over platinum black in a current of oxygen. A quantity of suboxide was formed from a portion of anhydride which had been heated at 230° during several hours, so that either this treatment was insufficient to remove all the phosphorus oxide (b. p. 173°), or the commercial anhydride contains small quantities of other lower oxides of phosphorus.   J. B. T.

The Yellow Modification of Arsenic. By J. W. RETGERS (*Zeit. anorg. Chem.*, **6**, 317—320).—In his previous paper (Abstr., 1893, ii, 570) the author had neglected to notice Schuller's work (*Math. u. naturw. Ber. aus Ungarn* (1889), **6**, 94), to which he now draws attention. Schuller sublimed pure arsenic in a vacuum, and obtained a *yellow* sublimate of arsenic, characterised by its extreme volatility and by its instability. He further calls attention to the parallel series of modifications of phosphorus and arsenic.

Phosphorus.	Arsenic.
(*a.*) Colourless, regular.	(*a.*) Yellow.
(*b.*) Light-red (? regular).	(*b.*) Black (? regular).
(*c.*) Dark-red to opaque, hexa- gonal, " metallic phos- phorus."	(*c.*) Silver-white, hexagonal.

C. F. B.

Potassium Arsenite Sulphate. By A. STAVENHAGEN (*Zeit. angw. Chem.*, 1894, 165—166).—The author, some time ago, investigated compounds of arsenic trioxide with sulphuric anhydride (Abstr., 1893, ii, 459), and has now succeeded in preparing a double salt of potassium sulphate with potassium arsenite. 21·8 grams of potassium sulphate and 3 grams of potassium ortharsenite were dissolved in 85 c.c. of water, evaporated to the crystallising point, and slowly left to crystallise. The double salt separated as small, lustrous prisms, showing hexagonal forms when viewed under the microscope. Analysis proved its formula to be $K_3AsO_3,10K_2SO_4$.   L. DE K.

Complex Acids: Condensation Products of Alkali Phos-phates or Arsenates with Chromates and Sulphates, and of Nitrates with Sulphates. By C. FRIEDHEIM (*Zeit. anorg. Chem.*, **6**, 273—302).—It has been shown, in the previous work on complex inorganic acids (Abstr., 1893, ii, 283), that these acids are not, as hitherto supposed, molecular compounds, but that they form complex molecules of definite atomic structure. For instance, the compound mentioned below as obtained from potassium dihydrogen phosphate and sulphuric acid, is to be regarded, not as $2K_2O,P_2O_5,2SO_3,3H_2O$, or as $KHSO_4,KH_2PO_4 + 2H_2O$, but as $OH \cdot PO(OK) \cdot O \cdot SO_2 \cdot OK + H_2O$. The evidence of this is manifold; these compounds cannot be obtained directly by crystallising a mixture of their constituents from water; they cannot themselves be recrystallised from water without undergoing decomposition; and the water, of crystallisation or of constitution, which they contain, is always lost either at a higher or at a lower temperature than is the case with the substances of which they might be regarded as molecular compounds; never at the same temperature.

These complex molecules always contain two acids corresponding with oxides of the types R_2O_5 and RO_3 respectively; and they are only formed when the latter acid is one capable of condensing with itself; as, for example, chromic acid, of which potassium dichromate, $OK \cdot CrO_2 \cdot O \cdot CrO_2 \cdot OK$, is a condensation product. The more nearly this acid approaches a base in character, the larger is the number of such condensation products which it will form, and the larger, too,

the number of its "complex" compounds. Thus, molybdic and tungstic acids are known to form many such compounds; chromic and sulphuric acids, which will condense, but not so readily, are now shown also to form complex compounds, but these are fewer in number. It is further shown that the acid oxide, R_2O_5, need not necessarily be V_2O_5, P_2O_5, or As_2O_5; it may even be N_2O_5. To conclude, in the author's words, "the composition of the so-called complex compounds, derived from acids R_2O_5 and RO_3, is closely dependent on that of the acid salts which the two acids are capable of forming, and on the more or less basic character of the trioxide."

A list is given below of the compounds described in the paper. The formulæ of these is contained in the middle column; in that to the left is given the constitution of the aqueous solution from which they were crystallised, and when some substance crystallised out of the solution before the complex compound in question, the formula of that substance is given in the right-hand column.

$KH_2AsO_4 : CrO_3$ $\}$ $As_2O_5 : K_2Cr_2O_7$ $As_2O_5 : (NH_4)_2Cr_2O_7$ $\}$	$OH \cdot AsO(OK) \cdot O \cdot CrO_2 \cdot O \cdot CrO_2 \cdot OK$	$K_2Cr_2O_7$
	$OH \cdot AsO(ONH_4) \cdot O \cdot CrO_2 \cdot O \cdot CrO_2 \cdot ONH_4$	$(NH_4)_2Cr_2O_7$
$NH_4H_2AsO_4 : CrO_3$	$AsO(ONH_4)(O \cdot CrO_2 \cdot O \cdot CrO_2\ ONH_4)_2$	
$P_2O_5 : K_2Cr_2O_7$ $\}$ $1 \cdot 5P_2O_5 : K_2Cr_2O_7$	$OH \cdot PO(OK) \cdot O \cdot CrO_2 \cdot O \cdot CrO_2 \cdot OK$	$K_2Cr_2O_7$
$P_2O_5 : (NH_4)_2Cr_2O_7$ $\}$ $NH_4H_2PO_4 : CrO_3$	$PO(ONH_4)(O \cdot CrO_2 \cdot O \cdot CrO_2 \cdot ONH_4)_2$	
$2KH_2AsO_4 : H_2SO_4$ $KH_2AsO_4 : H_2SO_4$	$OH \cdot AsO(OK) \cdot O\ SO_2 \cdot OK + H_2O$ $As(OK)(O \cdot SO_2 \cdot OK)_4 + 3H_2O$	$KHSO_4$
$2NaH_2AsO_4 : H_2SO_4$ $\}$ $NaH_2AsO_4 : H_2SO_4$	$OH \cdot AsO(ONa) \cdot O\ SO_2 \cdot ONa + H_2O$	$NaHSO_4$
$2NH_4H_2AsO_4 : H_2SO_4$ $NH_4H_2AsO_4 : H_2SO_4$	$OH \cdot AsO(ONH_4) \cdot O\ SO_2 \cdot ONH_4 + H_2O$ —	(NH_4HSO_4) (NH_4HSO_4)
$2KH_2PO_4 : H_2SO_4$ $\}$ $2H_3PO_4 : K_2SO_4$	$OH \cdot PO(OK) \cdot O \cdot SO_2 \cdot OK + H_2O$	
$2NH_4H_2PO_4 : H_2SO_4$	$OH \cdot PO(ONH_4) \cdot O \cdot SO_2 \cdot ONH_4 + H_2O$	
$2KNO_3 : H_2SO_4$	$OH \cdot NO(OK) \cdot O \cdot SO_2 \cdot OK$	
$2NH_4NO_3 : H_2SO_4$	$OH \cdot NO(ONH_4) \cdot O \cdot SO_2 \cdot ONH_4$	

C. F. B.

Some Properties of Carbon Bisulphide. By H. ARCTOWSKI (*Zeit. anorg. Chem.*, **6**, 255—259).—At 130° mercuric chloride is fairly soluble in carbon bisulphide. At 8°, 100 parts of saturated carbon bisulphide solutions of mercuric chloride, bromide, and iodide contain 0·030, 0·122, and 0·238 parts of the respective salts. The following salts, KCl, KBr, KI, KNO_3, K_2SO_4, $KSbO_3$, Na_2CO_3, Na_3PO_4, NH_4Cl, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, $AgNO_3$, AgI, $MgCl_2$, $MgSO_4$, CdI_2, $SnCl_2$, $PbCl_2$, PbI_2, $Pb(NO_3)_2$, CuI, $HgCl$, $ZnCl_2$, Cr_2Cl_6, Al_2Cl_6 are insoluble, and HgI and Fe_2Cl_6 only very slightly soluble. Boiling carbon bisulphide, however, dissolves $HgNO_3$, and also $Pb(NO_3)_2$ to a slight extent.

Sidot's method of purifying carbon bisulphide is the best. The liquid is shaken with mercury until all marked ethereal odour has

disappeared, decanted, and slowly distilled. It is best to purify only small quantities at a time, and these immediately before use. The pure liquid boils at 46·27°, under 756 mm. pressure, and is almost free from smell. It remains pure when kept at the ordinary temperature in the absence of light, air, and moisture, but under other circumstances very readily undergoes slight decomposition.

<div align="right">C. F. B.</div>

Sodium Peroxide. By T. POLECK (*Ber.*, **27**, 1051—1053).—The chemical behaviour of sodium peroxide is quite analogous to, but much more energetic than, that of the peroxide of hydrogen or barium. It reduces salts of gold, silver, and mercury to the metallic state, with evolution of oxygen; platinic chloride solution is only reduced after decomposition of the hydrogen platinochloride by the addition of a silver salt. Sodium peroxide precipitates ferric hydroxide from ferrous and ferric solutions, and manganese peroxide and cobalt oxide from manganese and cobalt solutions respectively; it reduces permanganic acid to manganese peroxide, and oxidises chromous oxide to chromic anhydride. With uranium salts, it yields sodium peruranate, $Na_4U_2O_8 + 8H_2O$, which is precipitated by the addition of alcohol, and sets free chlorine from hydrochloric acid; on prolonged boiling, the solution of the peruranate becomes red, evolves oxygen, and then deposits sodium uranate. Sodium peroxide rapidly oxidises the hydroxide and salts of bismuth to bismuthic acid, and immediately reduces potassium ferricyanide to the ferrocyanide; the latter reaction forms the basis of Kassner's method for estimating the peroxide (*Arch. Pharm.*, **228**, 182, 432). Iron and chromium, or manganese and chromium, may be separated and estimated by the use of sodium peroxide, since the chromium is oxidised to chromic anhydride, whilst the other metals are precipitated. Tin, antimony, and arsenic may also be separated by precipitating as sulphides with ammonium sulphide, evaporating off the excess of the latter, and oxidising the dissolved sulphides with sodium peroxide; the oxides of the metals may then be separated in the ordinary way. The oxidised product may be at once tested for arsenic by Marsh's method, which would be impossible if nitric acid had been the oxidising agent employed. The fusion of silicates and metallic minerals with a mixture of sodium carbonate and peroxide would lead to an excellent method for their analysis, if crucibles of porcelain, platinum, nickel, and silver were not considerably corroded during the process.

Sodium metaplumbate is formed by the action of the peroxide on lead oxide, in presence of water; the orthoplumbate could not be prepared. Iodine combines with the peroxide on heating, with formation of sodium periodate. It would seem that the peroxide might advantageously be used as an oxidising agent for organic substances; it does not act on alcohol, but ether inflames on contact with it.   W. J. P.

Note.—No reference is made to Fairley's work on sodium peruranate (this Journal, 1877, i, 139). According to the latter, the formula of the salt is $Na_4UO_8,8H_2O$.—[EDITORS.]

Sodium Nitride. By L. ZEHNDER (*Ann. Phys. Chem.*, [2], **52,** 56—66).—The author has observed that when sodium is introduced electrolytically into glass tubes, such as are used for illustrating Hertz experiments, a portion of the deposit is reddish-brown in colour, and in appearance closely resembles metallic copper. This is found to be due to the combination of nitrogen with part of the sodium, and probable formation of the compound, NNa_3. H. C.

Action of Water on Bicalcium Phosphate. By A. JOLY and E. SOREL (*Compt. rend.*, **118,** 738—741).—When crystals of hydrated bicalcium phosphate are thrown into boiling water they become opaque, and the liquid, which is acid to litmus but neutral to methyl-orange, contains monocalcium phosphate, whilst the insoluble matter, which has become amorphous, is almost pure tricalcium phosphate. The conversion into tricalcium phosphate is made complete by repeated treatment with boiling water.

If with a constant quantity of water the proportion of bicalcium phosphate to water is less than 10 grams per litre, the product seems to be a mixture, but it has not yet been completely examined ; if the proportion of bicalcium phosphate is higher than 10 grams per litre, the ratio of calcium oxide to phosphoric anhydride diminishes as the proportion of salt to water increases, and the product is at first a mixture, but when the proportion of salt exceeds 15 grams per litre the product is completely crystalline, and seems to consist of the compound $Ca_3(PO_4)_2,4Ca_2H_2(PO_4)_2 + 2H_2O$. The conversion of hydrated bicalcium phosphate into the anhydrous salt in presence of boiling water, is due to a chemical change in which tricalcium phosphate is an intermediate product. The complete change is rapid and complete only when the liquid is acid ; the salt is obtained in a state of purity by adding calcium chloride to a boiling solution of disodium phosphate and monosodium phosphate. In order to obtain pure hydrated bicalcium phosphate, the liquid must likewise be acid. When calcium chloride is precipitated by disodium phosphate, the product is at first gelatinous tricalcium phosphate, whilst the liquid is acid both to litmus and to methyl-orange. Gradually, however, the precipitate is converted by the action of the acid liquid into crystallised bicalcium phosphate, the change being more rapid the more concentrated the solution, but the addition of a further quantity of acid is necessary to make the change quite complete.

C. H. B.

Artificial Preparation of the Barium and Strontium Analogues of Apatite and of Basic-slag. By C. v. WOYCZYNSKI (*Zeit. anorg. Chem.*, **6,** 310—311).—By oxidising 1·88 grams of phosphorus with nitric acid, adding 26·24 grams of barium nitrate and 0·7 gram of 57 per cent. hydrofluoric acid, and carefully neutralising with ammonia, a granular precipitate was obtained, which, when recrystallised, showed the characteristic forms of apatite, and had the composition $3Ba_3(PO_4)_2,BaF_2$. An analogous strontium compound was prepared.

By fusing 14 grams of barium hydroxide with 4 grams of sodium hydroxide, as far as possible in the absence of air, and adding 5 grams

of sodium phosphate, the barium analogue $Ba_3(PO_4)_2,BaO$, of basic-slag was obtained in small, quadratic tables. The strontium analogue can be obtained in a similar way.   C. F. B.

Colloïdal Zinc Sulphide. By P. DONNINI (*Gazzetta*, **24**, i, 219—222).—It is well known that precipitated zinc sulphide may be washed with ammonium chloride solution without any turbidity of the supernatant liquid resulting; washing with pure water, however, causes an opalescence which cannot be removed by filtration. The author shows that this is due to part of the zinc sulphide assuming a colloïdal form in presence of pure water, whilst the addition of an ammonium salt to the solution renders the sulphide again insoluble.

The precipitate deposited on adding hydrogen sulphide to an ammoniacal zinc solution has the composition ZnS. After sweeping out as much hydrogen sulphide as possible from the opalescent colloïdal solution by passing a current of an inert gas through it, rather less zinc (64·8 instead of 67·0) remains in the solution than would correspond with the sulphur present, if the latter existed merely as zinc sulphide. The same conclusion is arrived at on precipitating the colloïdal sulphide by heating, determining the hydrogen sulphide evolved, and weighing the precipitated sulphide. The colloïdal sulphide might have the composition $5ZnS,H_2S$, although the hydrogen sulphide present is probably only mechanically retained by the cold solution.   W. J. P.

Thallium Triiodide. By H. L. WELLS and S. L. PENFIELD (*Zeit. anorg. Chem.*, **6**, 312—316).—By digesting thallium iodide and iodine with alcohol, and allowing the solution to evaporate over sulphuric acid, rhombic crystals of thallium triiodide, TlI_3, were obtained, isomorphous with those of the triiodides of rubidium and cæsium (Abstr., 1892, 773, and 1893, ii, 67); $a : b : c = 0·6828 : 1 : 1·1217$ for TlI_3; $= 0·6858 : 1 : 1·1234$ for RbI_3; $= 0·6824 : 1 : 1·1051$ for CsI_3. As the authors claim to have proved that the latter salts are molecular compounds, the same follows for thallium triiodide, in which compound thallium is then really univalent. As thallium exhibits so many analogies with the alkali metals, it was thought that it might possibly be a mixture of the two alkali metals, with atomic weights of about 170 and 220, that are missing in Mendeléeff's table. No separation could, however, be effected by fractional crystallisation of the nitrate.   C. F. B.

Action of Copper Sulphate and Sulphuric acid on Metallic Copper. By A. SCHUSTER (*Proc. Roy. Soc.*, **55**, 84—85).—The author gives details of some experiments performed a few years ago, but hitherto unpublished, which prove that when copper is placed in a copper sulphate solution containing free sulphuric acid, and the tubes exhausted of air, the diminution in the weight of the copper is quite insignificant compared to what takes place in the presence of air. A similar behaviour is noticed in sulphuric acid alone.   H. C.

Mercurous Sulphide. By U. ANTONY and Q. SESTINI (*Gazzetta*, **24**, i, 193—198).—Mercurous sulphide, Hg_2S, was described by Sef-

ström and by Brande, but their product was supposed by Guibourt and by Barfoed (*Jahresb.*, 1864, 282) to consist of a mixture of mercuric sulphide and mercury.

On passing a stream of hydrogen sulphide through potassium sulphate solution containing mercurous chloride or acetate in suspension, at −10°, a black powder consisting of mercuric sulphide and mercury is deposited. A mixture of dry hydrogen sulphide and carbonic anhydride, however, acts on pure, dry mercurous chloride at −10° with formation of mercurous sulphide; the carbonic anhydride is employed merely to dilute the hydrogen chloride evolved. Mercurous sulphide is also obtained by the action of dry hydrogen sulphide on dry mercurous acetate at −10°, no gaseous diluent being necessary in this case; the salt is stable at −10°, but decomposes into mercuric sulphide and mercury if the temperature rises above 0°. Mercurous sulphide may be distinguished from the mixture of mercuric sulphide and mercury by its behaviour towards a mixture of dry hydrogen chloride and carbonic anhydride. On passing these gases over the mixture containing the mercuric salt, no action occurs at either low or ordinary temperatures. At −18° the gas has practically no action on mercurous sulphide; at −12° the salt is slowly converted into mercurous chloride, whilst at 0° the conversion proceeds rapidly. Above 0° the action becomes more sluggish as the temperature rises, until at +18° no mercurous chloride at all is produced ; this is accounted for by the fact that the mercurous salt is completely decomposed into mercuric sulphide and mercury at this temperature.

Mercurous sulphide is a black powder which is not affected by the alkali hydroxides, ammonia, ammonium sulphide, or dilute nitric and hydrochloric acids below 0°; fuming nitric acid, however, rapidly oxidises it. It readily dissolves in sodium or potassium sulphide below 0°, giving a limpid solution which, as the temperature rises, deposits mercury in a very fine state of subdivision.　　　W. J. P.

Allotropic Changes of Iron. By G. CHARPY (*Compt. rend.*, 118, 868—870).—A number of bars of steel were subjected to tensile strain, and, at the same time, were heated at a definite temperature. It was found that although the breaking strain at first decidedly increases with the temperature and afterwards diminishes, the change which produces the rectilinear break (this vol., ii, 237) diminishes continuously, and the break disappears above a certain temperature. The curves representing the earlier stages are analogous to those representing changes of state at different temperatures.

The curves representing flexion and compression also show a rectilinear portion if the steel is annealed, but not if the steel has been tempered or subjected to cold-hammering.

The curve representing the effect of tensile strain is not materially affected by somewhat wide variations in the duration of the test.
　　　　　　　　　　　　　　　　　　　　　　　　　　　　C. H. B.

Combination of Molybdenum Dioxide and Bisulphide with Alkali Cyanides. By E. PÉCHARD (*Compt. rend.*, 118, 804—807).—

An acid solution of molybdenum dioxide can be obtained without the aid of metallic molybdenum, by adding potassium iodide to a solution of an alkali molybdate in excess of hydrochloric acid, and boiling for a long time, or by electrolysing a solution of ammonium molybdate in hydrochloric or oxalic acid. When the acid liquids are mixed with potassium hydroxide, hydrated molybdenum dioxide is precipitated. If a hot, strongly ammoniacal solution is electrolysed, a brown deposit forms very slowly on the negative electrode, and consists of hydrated molybdenum dioxide, and not of the hydrated sesquioxide as Smith has stated (*Ber.*, 1880, 753).

Molybdenum dioxide dissolves very easily in an aqueous solution of potassium cyanide, forming a strongly alkaline blue liquid, which after concentration deposits blue needles of the compound $MoO_2Cy_2,2KCy$, which can be purified by digestion with alcohol, in which it is practically insoluble. This compound is very soluble in water, and its blue solution is stable in presence of alkalis. When treated with dilute acids, it becomes brown; with concentrated acids, it yields hydrocyanic acid and a brown precipitate of the compound MoO_2Cy_2, and if the latter is left in contact with acids, it yields hydrocyanic acid and a solution of the dioxide, the change being accelerated by heating. With solutions of metallic salts, the solution of the blue double cyanides yields heavy precipitates having characteristic colours; bluish-white with lead, pale brown with copper, greenish-blue with mercuric salts, and dark brown with silver salts. The silver compound has the composition $MoO_2Cy_2,2AgCy$.

An acid solution of the dioxide when treated with hydrogen sulphide yields a reddish-brown precipitate of the bisulphide, and the latter dissolves readily in a warm solution of potassium cyanide forming a deep green liquid, which when concentrated yields slender, black needles of the compound $MoS_2Cy_2,2KCy$. It can also be obtained by boiling a solution of potassium thiomolybdate with an excess of potassium cyanide, until the red colour of the liquid has completely changed to green. When treated with hot acids, it yields hydrocyanic acid and molybdenum bisulphide. The green solution of the salt is precipitated by alcohol; with metallic solutions, it gives precipitates with characteristic colours, *e.g.*, green with lead salts, red with silver salts, brown with copper salts.

It is molybdenum dioxide that gives the characteristic red coloration with thiocyanates, but the author was unable to isolate the red compound. A mixture of potassium thiocyanate and acid potassium molybdate, which becomes purple when mixed with a strong acid, becomes deep yellow only with acetic acid, and when the liquid is concentrated it yields yellow prisms of the compound

$$Mo_3O_{10}K_2,KCNS + 4H_2O,$$

which is decomposed by water with separation of potassium trimolybdate. An analogous ammonium compound, stable in presence of acetic acid, but decomposed by water, can also be obtained. Both salts dissolve in dilute hydrochloric acid, forming an orange liquid, which gives the purple coloration characteristic of molybdenum dioxide when mixed with zinc and ether. C. H. B.

Mineralogical Chemistry.

Nickeliferous Iron Pyrites from Sudbury, Ontario. By T. L. WALKER (*Amer. J. Sci.*, [3], **47**, 312—314).—The principal nickel ore of the Sudbury district is nickeliferous pyrrhotite, but at the Murray Mine nickeliferous iron pyrites also occurs. Marcasite, magnetite, galena, copper pyrites, and nickeliferous pyrrhotite are the associated minerals. At first only massive specimens were found, but in 1893 several bright cubic crystals were obtained. Specific gravity, colour, lustre, and magnetic properties are the same as in ordinary iron pyrites. Analysis of undecomposed massive pieces yielded

Ni.	Fe.	S.	H_2O.	Cu.	Insoluble.	As.
4·34	39·70	49·31	0·10	trace	5·76	none

The mineral is thus iron pyrites, in which part of the iron is replaced by nickel, its composition being represented by the formula $(FeNi)S_2$. B. H. B.

Variscite from Utah. By R. L. PACKARD (*Amer. J. Sci.*, [3], **47**, 297—298).—A beautiful green mineral from a quartz vein near Lewiston, Utah, proved to have a composition the same as that of variscite, the analytical results being as follows.

H_2O.	P_2O_5.	Al_2O_3.
22·95	44·40	32·65

The mineral is compact or crypto-crystalline and dull. Its sp. gr. is 2·62, and its hardness about 4. B. H. B.

Analysis of a Molybdenum Mineral, and the Existence of a Ferrous Tetramolybdate. By M. SPICA (*Gazzetta*, **24**, i, 97—111). —The author has examined a crystalline quartzose rock from Stilo in Calabria; the several constituents of the rock were mechanically separated. It consisted of a siliceous gangue, biotite, and another mica, molybdenum bisulphide, iron pyrites with a little copper sulphide, anhydrous uranium molybdate, $U_2(MoO_4)_3$, ferrous tetramolybdate, FeO, $4MoO_3$, $8H_2O$, and another substance not yet completely examined.

The uranium trimolybdate occurs in yellow amorphous crusts, and has not previously been obtained either from natural or artificial sources. The ferrous tetramolybdate separated from a solution of the last above-mentioned constituent of the rock in hydrochloric acid; it is very sensitive to the action of light, and is deliquescent. It is very soluble in water, but less so in alcohol. W. J. P.

Enstatite and the Products of its Alteration. By K. JOHANSSON (*Zeit. Kryst. Min.*, **23**, 152—155).—The author gives the results of an optical and chemical investigation of unaltered enstatite, and of the bastite-like products of its alteration. The specimens of enstatite analysed were obtained from Almeklovdal, Söndmöre, and

from Ödegården, Bamle in Norway, and those of bastite-like material were from North America and from Kjörrestadkilen, Bamle.

B. H. B.

Leucite in New Jersey. By J. F. KEMP (*Amer. J. Sci.*, **47**, 339—340).—The author recently described (Abstr., 1893, ii, 539) a basic dyke near Hamburg, New Jersey, which has been thought to contain leucite. A subsequent exploration at Rudeville, near Hamburg, has proved that there actually is in Sussex County, New Jersey, a leucite dyke rock, associated with the elæolite-syenite, and that the determination of a piece of the earlier described dyke by E. Hussak in 1882 as leucite-tephrite, although based on altered material, is substantiated by the discovery of satisfactorily fresh material.   B. H. B.

Chemical Composition and Related Physical Properties of Topaz. By S. L. PENFIELD and J. C. MINOR, jun. (*Amer. J. Sci.*, [3], **47**, 387—396).—The chemical composition of topaz has never been satisfactorily settled. It occurred to the authors that perhaps the variations in the percentages of fluorine and the failure to yield a simple ratio are due to the partial replacement of fluorine by hydroxyl. Tests were accordingly made for water, and it has been found to be always present (compare Jannasch and Locke, this vol., ii, 284). The results of analyses of topaz from 10 localities show, as was anticipated, that fluorine has been replaced by hydroxyl, and the ratios indicate that $SiO_2 : Al_2O_3 : F + OH = 1 : 1 : 2$. In topaz, as in herderite, an increase in hydroxyl is accompanied by a decrease in specific gravity and an increase in the indices of refraction. In both minerals, the substitution of hydroxyl for fluorine causes a change in the lengths of the crystallographic axes.   B. H. B.

Analysis of Nepheline. By H. BERGHELL (*Zeit. Kryst. Min.*, **23**, 157 ; from *Geol. Fören. Forhand*, **13**, 300).—At Iiwaara in Finland, in a rock known as ijolite, nepheline occurs in an unaltered condition. On analysis it gave the following results.

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	Total.
43·98	34·93	0·36	16·76	3·83	99·86

B. H. B.

Milosin, Alexandrolite, and Avalite. By S. M. LOSANITSCH (*Chem. News*, **69**, 243—245).—Milosin and avalite are Servian minerals, the composition of which had hitherto not been established. A new green mineral occurring with milosin is termed alexandrolite by the author. Analysis of the three minerals gave the following results.

	SiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	MgO.	K_2O.	H_2O.	Total.
I.	76·37	30·18	9·75	0·91	trace	trace	13·76	100·88*
II.	52·07	20·76	13·74	2·22	trace	trace	10·88	99·67
III.	54·66	20·46	10·88	1·18	2·06	4·61	5·66	99·5]

I. Milosin ; II. Alexandrolite ; III. Avalite.

B. H. B.

* The figures given add up to 130·97. A formula suggested in the original for he mineral requires SiO_2, 45·35 per cent. only.

Phonolitic Rocks from Black Hills. By L. v. PIRSSON (*Amer. J. Sci.*, [3], **47**, 341—346).—In the Black Hills of Dakota, there is an extremely interesting series of high-alkali rocks. A phonolite from this region, described by the author, gave, on analysis, the following results.

SiO₂.	TiO₂.	Al₂O₃.	Fe₂O₃.	FeO.	MnO.	CaO.	BaO.	MgO.	Na₂O.
61·08	0·18	18·71	1·91	0·63	trace	1·58	0·05	0·08	8·68

K₂O.	H₂O.	Cl.	SO₃.
4·63	2·21	0·12	trace.

The sp. gr. is 2·582. The very small amount of bivalent metallic oxides present and the great excess of soda over potash are noteworthy. B. H. B.

Analysis of a Meteorite from Zabrodje. By P. MELIKOFF and L. PISSARJEWSKY (*Ber.*, **27**, 1235—1238).—This meteorite fell on September 22, 1893, at Zabrodje in the province of Wilna; it weighs 3155 grams, the sp. gr. = 3·71 at 20°. It contained considerable quantities of ferrous sulphide and nickel iron, NiFe₆ (Taënite), together with small crystals of ferrous chromate; 59·08 per cent. was soluble in hydrochloric acid. The silicates had the following composition.

SiO₂.	MgO.	CaO.	FeO.	MnO.	Al₂O₃.	Na₂O.	K₂O.	Total.
39·39	22·37	2·32	13·84	1·11	2·12	1·21	0·41	82·77

The composition of the meteorite was

NiFe₆.	FeS.	P₂O₅.	FeCrO₄.	Olivine.	Insoluble silicate.	Total.
9·31	6·6	0·19	0·7	42·77	40	99·57

The insoluble silicates probably consist of albite (11·26 per cent.) and of bronzite (28·74 per cent.). J. B. T.

Mineral Water of Gyrenbad. By F. P. TREADWELL (*Arch. Pharm.*, **231**, 579—591).—The upper spring of Gyrenbad (Canton Zürich) yields 10—15 litres of water per minute. The water is clear, colourless, and odourless. The temperature of the water on the 26th of February, 1893, was 8°, the temperature of the air being 5·2°; the sp. gr. was 1·00043 at 12·9°. The results were as follows in parts per 10,000.

Cl.	SO₃.	CO₂.	N₂O₅.	AlPO₄.	K₂O.
0·005561	0·065098	3·614400	0·010310	0·000200	0·010563

Na₂O.	(NH₄)₂O.	CaO.	BaO.	MgO.	SiO₂.
0·016237	0·003030	1·400600	trace	0·422190	0·060120

FeO.	Organic matter.	Total residue.
0·000054	0·066369	3·558050

CO₂ (free and half combined) 1180·2 c.c. at 8° and 770 mm.
CO₂ (free) 331·43 c.c. at 8° and 770 mm.

A centinormal solution of potassium permanganate immediately produced a pink coloration in 500 c.c. of the water acidified with sulphuric acid.   M. O. F.

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Physiological Chemistry.

Assimilation of Inorganic Substances. By J. NEUMANN (*Chem. Centr.*, 1894, i, 561—562 ; from *J. Landw.*, **41**, 343—380).—A calf was fed on milk, then for a second period on milk *plus* 9 grams of calcium phosphate, then for a third period on milk *plus* 12 grams of calcium phosphate daily ; the following results were obtained.

	1st period.	2nd period.	3rd period.
a. Lime.			
Taken in..........	24·63	27·38	29·19
Excreted..........	12·86	14·42	16·77
Assimilated	11·77	12·96	12·42
b. P$_2$O$_5$.			
Taken in..........	30·46	32·83	34·33
Excreted..........	14·91	16·87	18·39
Assimilated	15·55	15·96	15·94

That is, about 50 per cent. was assimilated in the first period, and the quantity absorbed varies but little, although the amount ingested was increased in the second and third periods, and so the percentage assimilated fell.

In another research, however, in which 7·5 grams of calcium carbonate was added to the milk, the quantity assimilated rose to 61 per cent.   W. D. H.

Digestibility and Nutritive Value of Margarine. By A. JOLLES (*Monatsh.*, **15**, 147—163).—From experiments on dogs, conducted in the usual way by comparing ingesta with egesta, the conclusion is drawn that margarine, so far as regards digestibility and nutritive value, is exactly similar to true butter.   W. D. H.

Proteïd Metabolism. By A. RITTER (*Chem. Centr.*, 1894, i, 592 ; from *Sitz. Ges. Morph. u. Physiol. München*, **9**, ii, 62).—Some recent observers have stated that human beings can maintain nitrogenous equilibrium on considerably less proteïd than was formerly stated to be necessary. The present research on two men, carried out in the usual way, does not confirm this. Both lost considerably both in weight and health ; the sparing action of fat and carbohydrate on proteïd metabolism is therefore limited.   W. D. H.

The Varieties of Sugar formed by Animal Ferments from Starch and Glycogen. By E. KÜLZ and J. VOGEL (*Zeit. Biol.*, 108—124).—The starch used was rice starch in a 5 per cent. solution. It was subjected to the action of the ferment, and the sugar formed identified by the use of the phenylhydrazine reaction; the osazone being subjected to elementary analysis.

As the result of the action of human parotid saliva, the sugar formed yielded isomaltosazone.

Mixed human saliva produced isomaltose at first, later, maltose was formed in addition, and even small quantities of dextrose.

Dogs' saliva gave rise to isomaltose.

Ox pancreas acted similarly.

The remaining experiments relate to glycogen. Human parotid saliva produced isomaltose and maltose in the proportion 1 : 2 from liver glycogen. From muscle glycogen, small quantities of the same saliva produced isomaltose, with small quantities of maltose and dextrose. Large quantities of the same saliva produced maltose only.

Ox pancreas and liver glycogen led to the formation of isomaltose with a very small admixture of maltose. Ox pancreas and muscle glycogen led to the formation of isomaltose with a very small admixture of dextrose. Diastase produced the same products from muscle glycogen.　　　　　　　　　　　　　　　　　　　W. D. H.

Chemical Changes in Cartilage during Ossification. By C. CHABRIÉ (*Compt. rend.*, 118, 1057—1060).—The process of ossification is usually regarded as a process in which the cartilaginous (chondrogenous) basis is replaced by osseous (gelatin-yielding) tissue. The present paper gives certain theoretical chemical reasons for believing that the change is not such a replacement, but an actual conversion of chondrogen into collagen.　　　　　　　　　　　　　W. D. H.

Protagon. By W. G. RUPPEL (*Zeit. Biol.*, **31**, 86—100).— Protagon was separated in a crystalline form from the brains of human beings and oxen. Elementary analysis gives numbers agreeing closely with those of previous observers, and thus the view of Gamgee and Blankenhorn, which is supported by Baumstark, that protagon is a chemical unit, is confirmed.

The following table gives the principal analyses hitherto made.

	Liebreich.	Gamgee and Blankenhorn.	Baumstark.	Kossel.	Ruppel.	
					Ox.	Human.
C	66·74	66·39	66·48	66·25	66·29	66·51
H....	11·74	10·69	11·12	11·13	10·75	10·88
N	2·80	2·39	2·35	3·25	2·32	2 55
P	1·23	1·068	1·02	0·97	1·13	1·138
S	—	—	—	0·51	0·096	—

　　　　　　　　　　　　　　　　　　　　　　　W. D. H.

Fats of Human Milk. By W. G. RUPPEL (*Zeit. Biol.*, **31**, 1—11).—The fatty acids found in human milk are butyric, caproic, capric, myristic, palmitic, stearic, and oleic acids all combined with glycerol. The presence of formic acid is also inferred from its reducing action, but not by any further tests. Quantitative analysis is not given, human milk is, however, poor in the volatile acids.

<div align="right">W. D. H.</div>

Crystalline Acids of Human Bile. By LASSAR-COHN (*Ber.*, **27**, 1339—1346).—The method previously employed by the author for the investigation of ox bile (Abstr., 1892, 1114; 1893, ii, 220) has now been applied to that of human bile. The bile was hydrolysed by boiling it for 24 hours with 6 per cent. potassium hydroxide, this concentration being maintained by the addition of water from time to time. The results may be summed up as follows:—There is obtained from human bile one more acid than from ox bile, namely, *fellinic* acid, $C_{23}H_{38}O_4$. This is a tasteless compound melting at 166—169°; it is homologous with choleïc acid, and apparently distinct from Schotten's fellenic acid (Abstr., 1887, 606). The other substances separated were cholic acid, $C_{24}H_{40}O_5$, choleïc acid, $C_{24}H_{40}O_4$, besides fatty acids and uncrystallisable resin.

<div align="right">A. R. L.</div>

Urea Formation. By A. GAUTIER (*Compt. rend.*, **118**, 902—904), by A. CHAUVEAU (*ibid.*, 904—906), by BERTHELOT (*ibid.*, 906—907), and by KAUFMANN (*ibid.*, 937—939).—It is admitted that urea is in great part formed in the liver from proteïd material. Chauveau regards this as due to oxidation, whilst Gautier considers that in the liver and other organs, urea is the product of fermentation (hydrolysis), and that oxygen is unnecessary. This he supports by stating that—(1) protoplasm is usually reducing in its action, and in the liver glycogen, sugar and fat are formed, by reduction, simultaneously with the urea; (2) Ehrlich's experiments with sodium sulphindigotate and other pigments show that the reducing action of living tissues during life is especially marked in the liver; (3) Richet's experiments show that urea is formed in a piece of liver plunged into melted paraffin where there can be no access of oxygen. In the two papers that follow the first, it is pointed out that the liver normally is being traversed by blood rich in oxygen, and that the formation of urea is on all fours with that of carbonic anhydride.

Kaufmann's paper relates to the site of urea formation, and the conclusions he draws from his experiments are—(1) that the formation of urea is not entirely localised in the liver; all other tissues produce a certain quantity; (2) nevertheless the liver is the seat of most active and abundant production of urea; (3) that this urea formation is produced by the interaction of the blood and by metabolic phenomena in the tissues.   W. D. H.

Chemical Composition of a Fatty Tumour. By W. G. RUPPEL (*Zeit. Biol.*, **31**, 101—107).—The results of the analysis may be briefly stated as follows.

	Grams.
Connective tissue	11·0 = 1·90 per cent.
Fat	452·0 = 78·07 ,,
Water...................	116·0 = 20·03 ,,
	——
Total weight	579·0

The 452 grams of fat contained :—

	Grams.
Free fatty acids...........	4·52 = 1·0 per cent.
Oleic acid	293·80 = 65·0 ,,
Fixed acids (mostly stearic)	166·22 = 23·5 ,,
Glycerol, volatile acids (especially capric and butyric), and unsaponifiable substance	47·46 = 10·5 ,,

W. D. H.

Poisoning by Pyrogallol and its Detection. By D. VITALI (*L'Orosi*, **17**, 37—45).—Death resulted from the administration of 0·20 gram of pyrogallol, in several doses, to a dog weighing 8 kilos. The phenol can be detected in the urine after the first dose, but not after subsequent doses, its oxidation products only being then found.

W. J. P.

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Chemistry of Vegetable Physiology and Agriculture.

Chemical Constituents of Ilex Paraguayensis.   By H. KUNZ-KRAUSE (*Arch. Pharm.*, **231**, 613—640).—The chemistry of the maté leaf has not been the subject of much investigation within recent years.   The author refers to caffeïne and tannic acid, together with proteïds and inorganic salts, as having already been shown by various chemists to occur in the leaf of the Brazilian holly, and then describes results which prove the presence of combined choline, an optically inactive sugar arising from the hydrolysis of the tannin present, and soluble potassium and magnesium salts, amounting to more than 1 per cent. of the dried leaf.   Brazilian holly does not contain ilixanthin.

The author has submitted the tannin derived from maté to a close comparison with that obtained from coffee, and is able to confirm Rochleder's conclusion that these two acids are identical.   This is shown by numerous reactions common to both, and also by the fact that hydrolysis, with concentrated potash, gives rise to the dihydroxycinnamic acid already obtained by Hlasiwetz from caffetannic acid (*Annalen*, **142**, 221 and 357).

Dihydroxycinnamic acid, $C_9H_8O_4$, [COOH : (OH)$_2$ = 1 : 3 : 4], separates from alcohol in pale-brown aggregates, single crystals from an aqueous solution being light yellow.   With bivalent metals it forms three series of salts—normal, monobasic, and bibasic.   Fusion

takes place at 197—201°, accompanied by evolution of carbonic anhydride; the residue most probably contains the hitherto unknown 3:4-dihydroxycinnamene, which shows the colour reaction with strong sulphuric acid characteristic of its methyl ether (Abstr., 1881, 740), and also yields catechol when submitted to dry distillation.

The tannin from maté is not readily attacked by hydrochloric acid, but bromine water is decolorised by its aqueous solution with the formation of bromodihydroxycinnamic acid, although the direct action of bromine on dihydroxycinnamic acid gives rise to a dibromo-derivative.

Another proof of the identity of the tannins derived from coffee and from maté is the decomposition of the latter by Liebermann's reagent, with the formation of glucose, catechol, oxalic acid, and hydrogen cyanide, the intermediate product being dihydroxycinnamic acid. The glucose from this source is an optically inactive syrup, which yields a crystalline osazone, and reduces Fehling's solution. Hence the occurrence of glucose in the aqueous extract of the dried leaf is explained by the decomposition of a portion of the tannin present.   M. O. F.

Balsam of Tamacoaré; a Brazilian Vegetable Oil. By F. PFAFF (*Arch. Pharm.*, **231**, 522—541).—Tamacoaré balsam is viscid, and of a yellowish-brown colour; it is heavier than water, with which it forms an emulsion, but is soluble in all other ordinary solvents. When distilled, either under atmospheric pressure or in a vacuum, it undergoes decomposition, and, although a clear oil passes over in a current of superheated steam, the distillate soon becomes brown as the temperature rises.

A study of the chemical properties of Tamacoaré balsam shows it to consist of an individual substance of the formula $C_{23}H_{34}O_5$. By mixing alcoholic solutions of the oil and mercuric chloride, a derivative of the composition $C_{23}H_{33}O_5,HgCl$ is obtained, crystallising in tufts of colourless needles, soluble in cold chloroform and ether, but insoluble in boiling alcohol. On passing hydrogen sulphide through a solution of the compound in ether and alcohol, to which a few drops of hydrochloric acid have been added, mercuric sulphide is precipitated, whilst the filtrate contains the original oil. One specimen of Tamacoaré balsam, after remaining in a stoppered flask for two years, deposited colourless crystals identical in chemical properties with the oil, which is regenerated by dissolving the crystalline product in any ordinary solvent (alcohol excepted), and evaporating.

Decomposition of the oil with concentrated alkalis gives rise to numerous products, of which, however, normal butyric and caprylic acids only have been identified.   M. O. F.

Blay-Hitam; a Malayan Arrow Poison. By H. SANTESSON and C. G. SANTESSON (*Arch. Pharm.*, **231**, 591—612).—The authors have submitted the bark of the Blay-Hitam plant to a careful examination, and have succeeded in isolating, as its chief chemical constituent, an alkaloïd which corresponds completely in chemical and toxic properties with brucine. The same alkaloïd is present in

the wood and sap, the latter also giving uncertain indications of the presence of strychnine.   M. O. F.

Composition of the Ash of Olive Mark Extracted with Water and with Carbon Bisulphide. By D. MARTELLI (*Staz. Sper. Agrar.*, **25**, 60—72).—The pasty substance obtained after the expression of the oil from olives is sometimes employed as cattle food or manure, or it is further extracted with water or with carbon bisulphide. The residue may be used as food or manure, and is frequently used as fuel for heating the kettles in the oil factories. Samples of ashes from various sources were obtained and analysed. There is a good deal of difference in the results, owing to the difference in the soils on which the olives were grown, and also to differences in the manner in which the olives were treated. The most valuable ashes, as manures, were those obtained from residues extracted with carbon bisulphide; the pure ashes contained K_2O, 19 to 32 per cent.; CaO, 16—33 per cent.; P_2O_5, 3 to over 5 per cent.; MgO, 3 to 3·7 per cent.; and SO_3, 1 to 10·7 per cent. The residues extracted with water gave less nutritive ashes, especially as regards potash (4·6—20 per cent.); phosphoric anhydride was also lower (3·7—4·3 per cent.). Chlorine, which was present in the ash from the carbon bisulphide residue to the amount of 0·5—4 per cent., was found only in traces in the ash of residues washed with water. The author points out the importance of utilising the ashes for manuring, either alone or mixed with nitrogenous matter, and sufficient acid to neutralise the alkali.   N. H. M.

Analytical Chemistry.

Laboratory Apparatus. By F. ANDERLINI (*Gazzetta*, **24**, i, 150—156).—In place of the ordinary Geissler potash bulbs used in organic analysis, the author recommends a modification in which three bulbs are arranged one above the other inside a fourth; the whole apparatus stands on a foot, and can be improved by the addition of a tap closing both entrance and exit tubes.

An improved form of calcium chloride drying tube for use in organic analysis is also described; it consists of a cylinder standing on a foot, and containing an internal tube down which the products of combustion pass. The whole apparatus is filled with calcium chloride, and both inlet and outlet are closed by a tap at the top of the apparatus. Towers, of somewhat similar construction to the preceding, may be advantageously employed in drying the air or oxygen used in the analysis.

The author also describes improved forms of fractionating columns and a safety separating funnel. W. J. P.

Estimation of Moisture in Wood Pulps. By J. C. BELL (*J. Soc. Chem. Ind.*, 1894, 117—118).—The author recommends that the sample should be dried to constant weight at 100°, and then a definite percentage of moisture allowed. The exact amount to be allowed should be fixed by a joint committee of manufacturers and analysts.

L. DE K.

Estimation of Sulphur in Sulphides, and Simultaneous Estimation of the Arsenic present. By P. JANNASCH (*Zeit. anorg. Chem.*, 6, 303—309).—The apparatus used is figured below. A is an apparatus for generating hydrogen chloride ; B contains sulph-

uric acid, and has a calcium chloride tube attached; the vessel *a, c, b, d, e, f* is of hard glass; *h* is a ground-glass joint ; *i* contains 3 per cent. aqueous hydrogen peroxide, with some strong nitric acid added; *l* and *m* the same mixture, diluted with an equal volume of water. About 0·6 gram of the finely-powdered mineral is placed in the vessel *a, f*, and first heated with a flat flame Bunsen burner for about half an hour in a current of dry oxygen; the sulphur and most of the arsenic are oxidised and carried over. The oxygen apparatus is then disconnected, and replaced by A, B; and *a, f* is immersed in boiling water, while a rapid current of hydrogen chloride is passed through for 1½—2 hours. The contents of *i, l,* and *m* are now mixed, and concentrated to 20—25 c.c., small quantities of strong nitric acid being added from time to time. The residue is diluted to 200 c.c., the sulphuric acid precipitated with a very slight excess of barium chloride, and the barium sulphate collected and weighed. The excess of barium in the filtrate is precipitated with a very slight excess of sulphuric acid, the filtered solution is evaporated to a small bulk, and made alkaline with ammonia, and the arsenic is then precipitated with a slight excess of magnesium chloride, the precipitate being treated as described in Abstr., 1892, 658.
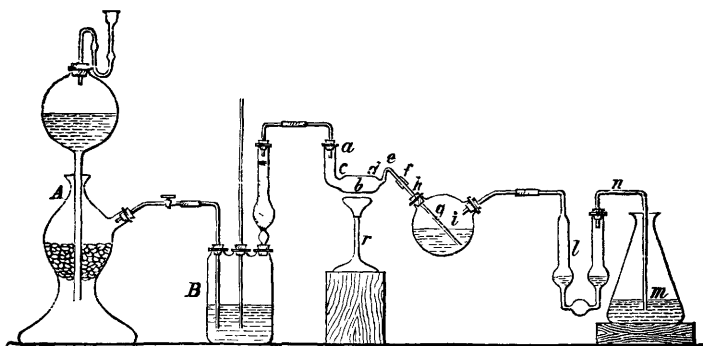
C. F. B.

Estimation of Arsenic in Copper. By F. PLATTEN (*J. Soc. Chem. Ind.*, 1894, 324—326).—The author, having satisfied himself that arsenious sulphide is completely decomposed by boiling with a

large amount of water, recommends the following process for the estimation of arsenic in copper.

The metal is heated, as usual, with ferric oxide and hydrochloric acid. The distillate is precipitated with hydrogen sulphide, and the impure arsenious sulphide is collected. Instead of directly weighing it, it is boiled for some time with about half a litre of water, and, after cooling, the arsenic is titrated with centinormal iodine solution in the usual manner.   L. DE K.

Detection of Arsenic when associated with Antimony and Tin. By F. A. GOOCH and B. HODGE (*Amer. J. Sci.*, [3], **47**, 382—385). —The mixture containing the three metals is distilled with 3 grams of potassium iodide dissolved in 5 c.c. of water and an equal volume of strong hydrochloric acid. The distillate is condensed in 10 c.c. of dilute hydrochloric acid (1 : 1). The free iodine is removed by the cautious addition of stannous chloride, and the arsenic is then precipitated by hydrogen sulphide. Traces of antimony, which may have passed over, and the added tin, are not precipitated in presence of such a large excess of acid. If it be desired to completely remove the arsenic, the residue in the flask must be distilled a few times more with hydrochloric acid. The remaining liquid is afterwards tested for tin and antimony in the usual manner.

The apparatus employed is essentially the one devised by Mohr, and consists of a 25 c.c. flask, fitted by means of a rubber stopper to a pipette, bent, drawn out at the lower end and dipped into a test tube, which is at the same time supported and cooled in a flask partly filled with water. The pipette tube should be wide enough to prevent the formation of bubbles within it, and the bulb large enough to retain any liquid which may happen to force itself back by accidental cooling of the flask.   L. DE K.

Testing for Boric acid in Wine-ash. By P. KULISCH (*Zeit. angw. Chem.*, 1894, 147—148).—Ripper, who first detected the presence of boric acid in the ash of wine, recommends that the mineral matter of 25—50 c.c. of wine should be dissolved in 10 c.c. of water and 2 c.c. of hydrochloric acid (sp. gr. 1·19). By means of faintly coloured turmeric paper, the boric acid reaction may then be readily obtained.

The author, however, recommends simply dissolving the ash in a few drops of acid, and testing with paper of a decided yellow colour. The test is then much more satisfactory.   L. DE K.

Estimation of Carbonic Anhydride in Presence of Soluble Sulphides. By A. WOLKOWICZ (*Zeit. angw. Chem.*, 1894, 165).— The author uses the apparatus recommended by Fresenius, but, before liberating the carbonic acid by means of hydrochloric acid, the substance is covered with a 20 per cent. solution of copper chloride. Copper sulphate must not be used, as this might form a cake of an insoluble sulphate and so prevent the proper action of the acid.

The hydrogen sulphide is completely retained by the copper solution, and the carbonic acid is dried and finally absorbed in weighed soda-lime tubes.   L. DE K.

New Method for the Volumetric Estimation of Magnesium.
By G. VENTUROLI (*Gazzetta*, **24**, i, 213—218).—On treating a solution
of a magnesium salt with disodium hydrogen phosphate, magnesium
hydrogen phosphate is formed ; this is converted, by boiling, into a
mixture of trimagnesium diphosphate and magnesium tetrahydrogen
diphosphate, $4MgHPO_4 = Mg_3(PO_4)_2 + MgH_4(PO_4)_2$. Since the
latter salt has an acid reaction, its quantity can be determined by
titration with standard alkali solution.

A concentrated aqueous solution, containing about 45 parts of
disodium hydrogen phosphate for every part of magnesia to be
estimated, is boiled, a little phenolphthaleïn being added ; during the
boiling, the neutral magnesium solution is run in until the red tint
vanishes. The solution is then titrated with decinormal soda solu-
tion until the red colour reappears, care being taken not to add soda
solution after the appearance of the pink tint. The quantity of mag-
nesium in the solution added to the phosphate can then be calculated,
knowing that 2 mols. of magnesia, MgO, are equivalent to 1 mol. of
soda, NaHO.

The process may also be employed for the estimation of calcium ;
the titration may be performed in the cold ; the reaction which occurs
is somewhat different : $5Na_2HPO_4 + 4CaCl_2 = 8NaCl + Ca_4H(PO_4)_3$
$+ 2NaH_2PO_4$. The tetracalcium hydrogen triphosphate separates
from the solution, and does not affect the analytical results ; 2 mols.
of lime, CaO, are equivalent to one of soda, NaHO.

Test analyses show that these methods possess considerable accu-
racy. A similar process is probably also applicable for the estimation
of barium and strontium.   W. J. P.

Estimation of Calcium and Magnesium. By O. FORTE
(*Gazzetta*, **24**, i, 207—213).—Calcium and magnesium may be esti-
mated, when in a solution containing no other metals, by precipitating
as carbonates, igniting, and weighing the mixed oxides ; the product
is then converted into sulphates, ignited, and again weighed.
                                                           W. J. P.

Valuation of Zinc Dust. By F. MEYER (*Zeit. angw. Chem.*, 1894,
231—232).—The author dissolves the sample in sulphuric acid and
measures the volume of the hydogen evolved. The apparatus consists
of a generating flask, a reservoir containing dilute sulphuric acid
(1 : 3), a graduated tube ending in a bulb with a stop-cock, and a con-
necting piece properly ground at each end and provided with a three-
way stop-cock.

1 gram of the zinc dust is put into the generating flask, which is
then fixed to the connecting piece and filled with water. After closing
the stop-cock, the other end is fixed to the graduated tube, and the
protruding end of the stop-cock is connected with the reservoir by
means of an india-rubber tube. The stop-cock on the bulb is now
opened, and the reservoir lifted up to fill the burette with acid, after
which the cock is again closed. By opening the three-way stop-cock
in the proper direction, the acid descends, in consequence of its
greater specific gravity, into the generating flask, and liberates hydro-

gen, which collects in the graduated tube, the liquid being driven back into the reservoir.

When the action is over, the liquids in the reservoir and burette are levelled, and the volume of the hydrogen is read off and corrected for temperature and pressure. The percentage of zinc in the sample is then found by a simple calculation. L. DE K.

Estimation of Cadmium. By M. MUSPRATT (*J. Soc. Chem. Ind.*, 1894, 211—213).—Cadmium may be accurately estimated as oxide, the ignition being effected in a stream of oxygen, but the oxide does not stand the heat of a gas blowpipe, suffering serious diminution in weight. The estimation as sulphide is also very good, but the precipitate is often difficult to filter and wash.

The preference, however, should be given to the electrolytic methods on account of their simplicity, cleanliness, and accuracy ; the chief precautions to be taken being the use of dilute solutions and weak currents. The metal is best deposited from a weak sulphuric acid solution, and it has little tendency to oxidise. L. DE K.

Estimation of Manganese in Minerals and Metals. By E. H. SANITER (*J. Soc. Chem. Ind.*, 1894, 112—116).—The author criticises the various gravimetric and volumetric processes. The weighing of manganese as Mn_3O_4 is utterly untrustworthy if the metal has been precipitated as hydrated dioxide ; somewhat better results are obtained when the precipitated sulphide is ignited in contact with air. The weighing as pyrophosphate is accurate if the solution has been completely freed from other metals, which is, however, a very tedious operation. Pattinson's volumetric process (titration of the dioxide with ferrous sulphate), and Volhard's method (titration with potassium permanganate), are trustworthy when the standard solutions are checked with manganese oxide of exactly known composition. L. DE K.

Estimation of Silicon and Aluminium in Iron. By L. L. DE KONINCK (*Chem. Centr.*, 1894, i, 523 ; from *Rev. univ. Mines*, **14**, 138). —The metal is first treated with nitric acid or nitro-hydrochloric acid, and precipitated with ammonia or ammonium hydrogen carbonate ; if manganese is present, the iron must be precipitated with ammonium acetate. The ammonia should be free from silica ; if not, it should be distilled, and the vapour condensed in the iron solution. The precipitate, after being collected on a filter, washed, and ignited, is placed in a weighed platinum boat and heated in a current of hydrogen chloride ; the iron is then volatilised as chloride, whilst silica and alumina remain behind. To estimate the aluminium, the mixture is evaporated with hydrofluoric acid, or ignited with ammonium fluoride, which causes the silica to volatilise. The aluminium may contain other substances such as titanium and chromium, and must, therefore, be further tested. L. DE K.

Acidimetric Estimation of Substances that form Molecular Compounds with Picric acid. By F. W. KÜSTER (*Ber.*, **27**,

1101—1105).—A strong flask is used, with an indiarubber stopper, through which passes a piece of glass tubing closed at the lower end, and with a small hole in the side rather above this end. It is thus possible to exhaust the flask, and then, by drawing up this tube until the hole is covered by the cork, to preserve a vacuum in the flask after the connection with the pump is broken. The substance to be examined is placed in the flask with a moderate excess of picric acid solution; this is a solution saturated at the ordinary temperature and of about N/20 strength. The flask, which should be filled about up to the neck, is then exhausted, and the whole heated on the water bath until all the substance has disappeared. It is then left for several hours, when the cold solution is filtered, and the excess of picric acid determined in the filtrate by titration with N/10 baryta water, phenolphthaleïn being used as an indicator. Good results were obtained with naphthalene, acenaphthene, and α- and β-naphthol; in the last case a correction had to be made for the picrate remaining in solution (100 c.c. of the picric acid solution dissolves 0·0075 gram β-naphthol). With phenanthrene, quantitative results could not be obtained. C. F. B.

Volumetric Sugar Estimations. By SAMELSON (*Zeit., angw. Chem.*, 1894, 267—268).—The gravimetric estimation of sugar by means of Fehling's solution has lately been again recommended instead of the volumetric process on account of its supposed greater accuracy.

The author thinks, however, that the volumetric process may be advantageously employed instead, if only the precaution be taken to ascertain the real titre of the alkaline copper solution, and not to blindly trust to its supposed strength. L. DE K.

Estimation of Acidity in Gastric Juice. By J. J. KASASS (*Chem. Centr.*, 1894, i, 481; from *Pharm. Zeit. Russ.*, 33, 21—22).—On adding hydrochloric acid to potassium hydrogen tartrate, the total acidity of the liquid is increased, owing to the liberation of the soluble tartaric acid. If the acidity of the mixture before the addition of the tartrate is called a, and that after, b, then $3(b - a) =$ free hydrochloric acid. Organic acids and proteïds do not interfere with the reaction. It may be applied to the estimation of hydrochloric acid in gastric contents, thus: 10 c.c. of the juice is titrated with sodium hydroxide (a); 12 c.c. is mixed with 6 c.c. of 95 per cent. alcohol, and excess of tartrate added, the mixture being allowed to remain an hour, and then filtered. 15 c.c. (= 10 c.c. of gastric juice) is then titrated as before (b). A third titration in a control specimen is necessary, as potassium hydrogen tartrate is not insoluble in alcohol (c). The quantity of free hydrochloric acid = $[(b - c) - a] \times 3$.

The results obtained come near to Günzburg's; after Ewald's test breakfast, the percentage of hydrochloric acid in the human stomach is 0·02 to 0·04. The results came out lower than Sjöquist's, by whose method the acid united to proteïds is also estimated. W. D. H.

Estimation of Essential Oils, especially in Oil of Cloves and Oil of Mace. By W. LENZ (*Zeit. anal. Chem.*, **33**, 193—200).—The following is suggested as an improvement on older processes for estimating the amount of oil obtainable from the spice:—10 to 20 grams of the powder is mixed with water in a 200 c.c. retort, the beak of which is inclined upwards, but at its middle is bent downwards at a right angle and connected with a condenser. 10 c.c. of olive oil is added to prevent frothing, and steam is passed through the mixture as long as any oil distils. The distillate, amounting to about 500 c.c., is saturated with sodium chloride and extracted by shaking with ether (50 c.c., three times). The ethereal solution is dried by digesting with 20 grams of fused calcium chloride for at least three days, and is then evaporated below 30° in a tared flask, through which a current of dry air is passed, until, at intervals of five minutes, its weight becomes constant. The percentage of eugenol in the oil is then determined by Thoms' method (Abstr., 1892, 250). The high solubility of oil of cloves in a 50 per cent. aqueous solution of sodium salicylate led to experiments in which this solution was substituted for water in the retort. The average yield of oil from the water distillations was 17·75 per cent., containing 79·44 per cent. of eugenol, from the salicylate 19·45 per cent., containing 84·52 per cent. of eugenol, the latter yield agreeing better than the former with that obtained on the large scale. Similar experiments with mace, the oil of which is nearly insoluble in salicylate solution, gave one-fourth more oil with the salicylate than with water, and that the action is not due to a mere rise in the boiling point of the solution is shown by the fact that solutions of potassium acetate and of calcium chloride have no such effect. The behaviour of the salicylate seems rather to be due to its peculiar solvent action on the plant tissues, which renders it such a valuable liquid for mounting microscopic preparations. M. J. S.

Detection of Adulteration in Lard. By SAMELSON (*Zeit. anal. Chem.*, **33**, 189—192).—A qualitative method for the detection of vegetable fats has long been a desideratum, and several such have been proposed, but neither Becchi's, Gantter's (Abstr., 1893, ii, 440), nor Welmans' can be depended on in all cases, the two former sometimes failing to give any indication in cases of undoubted falsification, whilst the latter may give as distinct a coloration where the purity of the sample is unquestionable, as in cases of adulteration. The iodine absorption remains at present the only trustworthy test.

M. J. S.

Detection of Cotton-seed Oil in Lard. By E. J. BEVAN (*Analyst*, **19**, 88—89).—The author examined a sample of genuine lard which, however, gave a decided silver reaction. By scraping off the top portion and taking a part of what lay underneath, to which the air had not penetrated, no silver reaction was obtained. The same result was obtained with bladder lard, and here the possibility of any mechanically deposited dirt being present was out of the question. Lard was then exposed in a still room in flat dishes, and after a week's exposure, it gave the reaction quite strongly. The

author can come to no other conclusion than that the effect observed is due to an oxidation process. After passing air for a few days through melted lard, a product was obtained which gave an intense reaction with silver solution. The substance formed is no doubt present in very minute amount, but there is quite enough to mislead, and give the impression that cotton-oil is really present.

L. DE K.

Estimation of Moisture and Oil in Linseed Cake, &c. By A. P. AITKEN (*J. Amer. Chem. Soc.*, **16**, 114—122).—In estimating moisture by drying the sample in a water oven, it is generally found several per cent. too low, and this, of course, spoils the estimation of the oil; the common practice being to determine the moisture in one part of the sample and the joint moisture and oil in another portion.

The author has now greatly improved the process by drying the sample, contained in an aluminium boat, at 100° in a current of dry coal gas, previously brought to the same temperature. By this means, oxidation of the oil is prevented. The oil is estimated by introducing the dried sample into an extraction tube, which is closed at the beginning of the elongated end with a double wad of filter paper, and after any powder adhering ·to the sides has been brushed down, another wad is patted in on the top. The tube is now inserted in one of the holes of a zinc box, which is filled with warm water. The narrow end of the tube dips into a weighed flask, in case it be desired to check the result by a direct weighing of the oil. Ether is now poured into the tube and the tube is corked; when the ether begins to boil it rapidly runs into the flask. The extraction is repeated 15 to 20 times. The contents of the tube are now pushed by means of a thin glass ramrod into a weighed aluminium capsule; the wads are cleaned with a camel-hair brush, and after drying the exhausted powder for a short time at 100°, it is reweighed.

L. DE K.

Estimation of Glycocine. By C. S. FISCHER (*Zeit. physiol. Chem.*, **19**, 164—178).—It is recommended that albuminoids, like gelatin, keratin, &c., may be estimated by the amount of amido-acids (glycocine, leucine, glutamic acid, &c.) formed from them. The present paper relates, however, to gelatin and the glycocine formed from it.

The glycocine is estimated by converting it, by the use of hydrochloric acid and benzoic chloride, into hippuric acid, which is crystallised out and weighed. Leucine, &c., may be estimated by forming similar benzoyl compounds.

W. D. H.

Detection of Horse-Flesh. By BRÄUTIGAM and EDELMANN (*Chem. Centr.*, 1894, i, 485; from *Pharm. Centr.-H.*, **35**, 60—68).—This method of detecting horse-flesh depends on the fact that this form of meat contains 0·373 to 1·072 per cent. of glycogen, whilst that of other animals used as food contains none, or the merest trace. Ox flesh comes next to horse-flesh (0·204 per cent.). From this, the authors claim to be able to detect 5 to 10 per cent. of horse-flesh mixed with other meat. The same holds for horse liver used in sausages.

W. D. H.

General and Physical Chemistry.

Spectrum of Oxygen at High Temperatures. By J. JANSSEN (*Compt. rend.*, **118**, 1007—1009).—When oxygen under various pressures is enclosed in a steel tube 10 m. long, provided with glass ends, and heated by means of a row of gas burners, the bands and lines of the spectrum show no appreciable variation between the ordinary temperature and 300°, but the gaseous column becomes distinctly more transparent to the spectrum as a whole.

When the oxygen is heated by means of a spiral of platinum wire enclosed in the tube and made incandescent by an electric current, no variations in the spectrum are observed in a tube 2·1 m. long with pressures reaching 100 atmos. and temperatures as high as 800—900°.

C. H. B.

Symbol for denoting the Optical Activity of Compounds. By H. LANDOLT (*Ber.*, **27**, 1362—1364).—Ladenburg has recently stated (this vol., i, 307) that the rotatory power of *d*-coniine is $[\alpha]_D$ = 15·6, and he draws attention to the fact that Landolt (*Das optische Drehüngs-vermögen*, 1879, 225) gives the value 17·9 on the authority of Schiff. Landolt, in reply, states that he, having observed that the natural base had a rotatory power of 15·6° in a 1 decimetre tube, concluded that Schiff's value was merely the observed angle, and accordingly divided this number by the sp. gr., using the value observed by Schiff, namely, 0·873 at 15°; he thus obtained 17·9 as the specific rotatory power. Schiff is unable to say definitely, but he believes that the value given by him (15·6°) had already been divided by the sp. gr. It is, however, to be observed that Schiff's value for the sp. gr. of the base, as to the accuracy of which he is certain, differs from that of Ladenburg (*loc. cit.*).

It is suggested that, to prevent confusion, authors shall employ the words "observed angle" and "specific rotatory power," the latter being taken in Biot's sense and denoted by the symbol $[\alpha]$, a small letter being affixed to indicate the particular light employed.

A. R. L.

Specific Rotation of Dissolved Substances. By A. AIGNAN (*Ann. Chim. Phys.*, [7], **1**, 433—463).—If an optically active substance A having the rotatory power $[a]$ is dissolved in presence of an inactive substance B and a compound of A and B having the rotatory power $[\alpha]$ is formed in the solution, it is evident, as Biot showed, that the rotatory power of the solution should show a point of discontinuity when the concentration attains a certain magnitude. For, suppose the solution to contain P of A and Q of B, and the ratio between the weights of A and B in the compound which they form to be n; further let ω be the rotation of a column of solution of thickness l and density δ, and let the weight M of the solution be constant, then when $Q < n P$

$$[\alpha] + \frac{[a]\,(n+1) - [\alpha]}{n} \cdot \frac{Q}{P} = \frac{M\omega}{Pl\delta},$$

and when $Q > nP$

$$(n + 1)\,[\alpha] = \frac{M\omega}{Pl\delta}.$$

Since $[a]$, $[\alpha]$, and n are constants, it is seen that the values of $\frac{M\omega}{Pl\delta}$ expressed as a function of Q/P are represented by the co-ordinates of two straight lines cutting each other. When $Q < nP$ or A is in excess the curve is a straight line inclined to both co-ordinates x and y; when $Q > nP$ or B is in excess, the specific rotation is independent of the excess of B and the curve runs parallel to one co-ordinate x. The author shows, however, that these two straight lines are merely tangents to the actual curve at the points where $x = 0$ and $x = \infty$, because a further complication is introduced into the question by dissociation brought about by the solvent itself; the influence of this may be readily investigated theoretically, and the results are shown to be concordant by series of determinations of rotatory powers of pinene in various solvents and of solutions of sugar and potash in water. The calculated and observed numbers agree very closely indeed. The co-ordinates of the point of intersection of the two tangents to the curve give the composition of the compound of A and B; this, in the case of sugar and potash, consists of 2 mols. of the latter to 1 of the former.

The author concludes with a discussion of the work of Biot and Gernez on optically active solutions, and shows that the experimental results are in complete agreement with his own theoretical ones.

<div align="right">W. J. P.</div>

Fluorescence. By E. BUCKINGHAM (*Zeit. physikal. Chem.*, **14,** 129—148).—Experiments were made to establish a connection between the phenomena of fluorescence and the ions present in the liquid. In the case of eosin, which contains acidic hydrogen, dilution increased the fluorescence; an addition of strong acids, that is, of hydrogen ions, caused it to diminish, as did also neutral salts if in sufficient quantity; strong alkalis also caused a decrease, probably owing to the formation of slightly dissociated salts. A few observations were made with β-naphthylaminedisulphonic acid, $[(SO_3H)_2\colon NH_2 = 1\colon 4'\colon 2]$, and then a large number with quinine. This compound being a feeble base, the effect of alkalis on solutions of its salts should be to diminish the fluorescence which should be increased by acids and strongly dissociated neutral salts, and the observed results were as expected. The experiments also show that the bivalent quinine ion, as in Q,SO_4H_2, is more strongly fluorescent than the univalent ions as in Q,HNO_3. Halogen ions exert a peculiar diminishing influence, which, although well marked and regular, the author is unable to explain. He considers, however, his results certainly indicate that fluorescence is an ionic phenomenon.   L. M. J.

Electrolysis. By O. WIEDEBURG (*Zeit. physikal. Chem.*, **14,** 174—180).—The paper contains a consideration of the question whether a certain maximum E.M.F. is required before electrolysis can be effected. The author considers that with any electromotive

orce (A) there corresponds a certain pressure (p) of the gaseous product according to the equation $A_1 - A_2 = c \log\frac{p_1}{p_2}$, and hence is of opinion that by any electromotive force, however small, electrolysis is set up. The ratio of current to E.M.F. is given by a curve consisting of two straight lines connected by a short curve, approximately a hyperbola. Where the curve is very short, an apparent break occurs, the position corresponding with the maximum of polarisation.

L. M. J.

Conductivity of Solutions. By N. STRINDBERG (*Zeit. physikal. Chem.*, **14**, 161—162).—The experiments of Arrhenius (Abstr., 1892, 1038) and Holland (Abstr., 1892, 1382) on the effect of a non-electrolyte on the conductivity of a solution, lead in both cases to the expression $l = l_0\left(1 - \frac{ax}{2}\right)^2$ but the constant a differs greatly in the two sets of experiments. The author therefore redetermines this constant, using solutions of sodium and cuprous chlorides, with acetone and ethylic alcohol as the non-conductors. The results obtained agree well with those of Arrhenius, but differ from those of Holland to the extent of from 24 to 56 per cent. L. M. J.

Electrical Conductivity of some Salts in Ethylic and Methylic Alcohol. By B. VÖLLMER (*Ann. Phys. Chem.*, [2], **52**, 328—356).—The conductivities of the acetates and iodides of sodium and potassium, and of lithium chloride, dissolved in ethylic and methylic alcohols were measured, as also those of the chlorides of sodium and calcium, and the nitrates of silver and calcium, dissolved in ethylic alcohol.

The molecular conductivities increase with increasing dilution, and approach a limiting value for infinite dilution, except in the case of calcium chloride and of calcium nitrate. The limiting values for the molecular conductivities in methylic and ethylic alcohol solution may be obtained from those in aqueous solution by multiplication with a factor, in the first case about 0.73, and in the second about 0.34. It appears, therefore, that the conductivity decreases with the rising molecular weight of the solvent. The temperature coefficients increase with rising dilution, and for very dilute solutions the conductivity coefficients are practically the same as those for the viscosity of methylic and ethylic alcohols. Ostwald's dilution law is not applicable to the solutions examined, and from the conductivities it is not possible to calculate the rise in the boiling point of ethylic alcohol in its solutions, as it is with water. H. C.

Determination of Critical Temperatures by means of the Critical Index of Refraction. By J. CHAPPUIS (*Compt. rend.*, **118**, 976—977).—The author has employed the observation of interference bands as a means of following the changes in the refractive index of a liquefied gas near and at its critical temperature. The liquid is placed in a cylindrical cavity in a steel prism, provided with apertures covered with optically-worked glass plates and surrounded by

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a liquid, the temperature of which can be controlled. Two beams of light produced by a pair of Jamin mirrors, starting from a Billet compensator, pass through the liquid in the prism, and through the surrounding bath, the sides of which are made of plates of optically-worked glass.

In the case of liquefied carbonic anhydride, the bands remain stationary and the refractive index is constant; beyond this temperature the bands fall and the refractive index increases rapidly. The curve of the indices at $31.61°$ shows a vertical tangent, and the intersection of this curve with the right line representing the index above this temperature is the critical point of the index. The results vary only between $31.60°$ and $31.62°$ (uncorr.), and the corrected value for the critical point as thus determined is $31.40°$, which approaches closely to Amagat's value, $31.35°$.　　　　　C. H. B.

Electrical Method for the Determination of Transition Points. By E. COHEN (*Zeit. physikal. Chem.*, **14**, 53—92).—If a voltaic element be formed by the immersion of similar electrodes in saturated solutions of the two forms of a substance capable of undergoing a transition change, then at temperatures above or below that of the transition, the current will flow in opposite directions, becoming *nil* at the transition temperature itself. This forms the basis of the method; such an element being placed in a thermostat, and the current measured at various temperatures, the null point being carefully determined. Details of the method and of the mode of preparing the element and the electrodes are given in the paper. The method is applicable to transition changes due to loss of water of crystallisation, formation of double salts, double decomposition, and polymorphism. The following changes are examined and the temperature determined:—

(1.) $Na_2SO_4,10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$. $t = 32.8°$.

(2.) $CdCl_2,2H_2O \rightleftharpoons CdCl_2,H_2O + H_2O$. $t = 34.1°$.

(3.) $ZnSO_4,7H_2O \rightleftharpoons ZnSO_4,6H_2O + H_2O$. $t = $ about $42°$.

(4.) $Na_2SO_4,10H_2O + MgSO_4,7H_2O \rightleftharpoons Na_2MgSO_4,4H_2O + 13H_2O$.
$t = 20.8°$.

(5.) $2MgSO_4,7H_2O + 2NaCl \rightleftharpoons MgNa_2(SO_4)_2,4H_2O +$
$MgCl_2,6H_2O + 4H_2O$ (good results were not obtainable).

The author points out that the method has the advantages of accuracy and speed, but is only applicable to conductors, whilst for some of these the preparation of the electrodes is a matter of very great difficulty. The paper concludes with a consideration of the method from the thermodynamical standpoint, the fundamental equation

$$E = W + T\frac{dE}{dt},$$

being applied for this purpose.　　　　　L. M. J.

Thermal Changes involved in the Formation of Amido-Acids and of Nitriles. By F. STOHMANN and H. LANGBEIN (*J. pr. Chem.*, [2], **49**, 483—501).—The following values are given:—

	Heat of combustion. Cal.	Heat of formation. Cal.
Glycocine, $NH_2 \cdot CH_2 \cdot COOH$	234·6	125·9
Diglycolamidic acid, $NH(CH_2 \cdot COOH)_2$	396·3	221·2
Triglycolamidic acid, $N(CH_2 \cdot COOH)_3$	560·0	314·5

It will be seen that the mean difference between the heats of combustion for each $CH_2 \cdot COOH$ group introduced is 162·7 Cal. If this be also the difference between the heat of combustion of glycocine and that of solid ammonia, the latter value must be 71·9 Cal. The heat of combustion of gaseous ammonia is 90·6 Cal., and the heat of vaporisation of ammonia is 5·4 Cal. The heat of liquefaction of ammonia is not known, but a value for this which would reduce the heat of combustion to 71·9 Cal. can hardly be entertained as probable. Ammonia may stand in the same relationship to glycocine as that which has been shown to exist between formic and acetic acids and between oxalic and malonic acids; that is, ammonia may be more energetic than glycocine. The heat of combustion of hypothetical liquid ammonia devoid of chemical energy may be taken at 90·6 − (5·4 + 12·3) = 72·9 Cal., for the heat of neutralisation of aqueous ammonia by aqueous hydrochloric acid is 12·3 Cal. On the basis of this value for ammonia, the author calculates the thermal values for the formation of glycolamidic acids by the interaction of ammonia and acetic acid, hydrogen being eliminated. The following conclusion may be drawn:—A hydrogen atom which enters into combination with a nitrogen atom effects a smaller increase of energy than when it enters into combination with a carbon atom (compare the variation in the heat of combustion produced by a methyl group under the same circumstances, Abstr., 1892, 6; 1893, ii, 362). It can also be shown from the author's figures that more energy must be supplied for the formation of a compound in which a carbon atom is attached to a nitrogen atom, than is necessary when the carbon atom is attached to another carbon atom. Thus it happens that the substitution of $CH_2 \cdot COOH$ for H increases the heat of combustion by 162·7 Cal. when the H is attached to nitrogen, and by 150·9 Cal. when it is attached to carbon.

The thermal changes concerned in the conversion of amines into amido-acids are next considered, and passing to the nitriles the following figures appear:—

	Heat of combustion. Cal.	Heat of formation. Cal.
Diglycolamidic nitrile, $C_4H_5N_3$	590·8	−42·3
Triglycolamidic nitrile, $C_6H_6N_4$	846·2	−75·2

The thermal changes involved in the formation of the nitriles from the acids, and in the hydrogenation, hydrolysis, and formation of the nitriles are also considered. A. G. B.

Salt Formation in Alcoholic Solutions. By C. M. VAN DEVENTER and E. COHEN (*Zeit. physikal. Chem.*, **14**, 124—128).—The

authors extend their previous experiments (Abstr., 1890, 553; 1892, 262) to the neutralisation, by an acid, of sodium dissolved in mixtures of water and alcohol. In the case of hydrogen chloride, the heat of neutralisation diminishes from 100 per cent. to about 90 per cent. alcohol, increasing however with additional water content. A similar result obtains when the solution is neutralised by hydrogen bromide, but with acetic acid no minimum results, the value continuously increasing on addition of water. The authors explain these results by the assumption that three kinds of reaction occur— (1), $HCl + NaC_2H_5O = NaCl + C_2H_6O$ (undissociated); (2), $HCl + NaOH = NaCl + H_2O$ (undissociated); and (3), $H/Cl + Na/OH = Na/Cl + H_2O$ (dissociated). In the case of the halogen acids, the heat of neutralisation is smallest for the second class, but with acetic acid, for the first class. They point out finally the importance of extended accurate observations where minima occur, in order to obtain data of the thermal effects for undissociated compounds.   L. M. J.

Corresponding Solutions. By G. TAMMANN (*Zeit. physikal. Chem.*, 14, 163—173; compare this vol., ii, 224, 268).—The author has previously shown that the thermal expansion of a solution at ordinary pressure corresponds with that of the solvent at a pressure Δk. Some cases of mixed solutions are examined, thus the values for Δk in the case of various solutions of potassium and sodium chlorides are given, and the expansion corresponding with the mean Δk is calculated, and found in most cases to agree well with the observed expansions of the mixed solutions. The concentration of solutions of the same salts, at which the values of Δk are equal, are also given, and found to agree well with Bender's "corresponding volumes; similar data being also given for the chlorides of lithium, barium, and ammonium. Such solutions should exhibit no volume alteration on mixing. Only in a few cases, however, are corresponding solutions also isohydric, examples of such cases being the carbonates and sulphates of sodium and potassium, in which the corresponding solutions are equimolecular. The sp. gr. of a mixture of equal quantities of these solutions therefore is the mean of the sp. gr. of the components, whilst they all exert the same effect in lowering the temperature of maximum density.   L. M. J.

Determination of the Reduction of the Freezing Points of Solutions. By A. PONSOT (*Compt. rend.*, 118, 977—980).—Regarding the freezing point of an aqueous solution as the temperature at which it is in equilibrium with ice, the author brings the solution in contact with an excess of finely-divided ice, agitates the mixture in a vessel carefully protected from radiation, reads the constant temperature, and pours off the liquid and determines its composition. The advantages claimed are that the liquid can contain no ice in superfusion, no correction is necessary for the concentration, and the temperature that has to be read off is stationary. A detailed description of the apparatus employed is given; the vessel containing

the solution is surrounded on all sides by jacketed cylinders containing mixtures at temperatures approximating to 0°. C. H B.

Relation between Depression of the Freezing Point and Osmotic Pressure of Solutions. By C. DIETERICI (*Ann. Phys. Chem.* [2], **52**, 263—274; compare this vol., ii, 228).—In answer to Arrhenius, the author admits the greater accuracy of Juhlin's observations on the vapour pressures of ice and water at temperatures below 0° as compared with those of Fischer, but still maintains that no strict proportionality exists between the depression of the freezing point and the osmotic pressure of solutions. The theoretical relationship existing between these two quantities is deduced, and it is shown that the assumption hitherto made, that the heat of dilution of dilute solutions is so small that it may be neglected, is incorrect.
H. C.

Variations in the Viscosity of Fused Sulphur. By J. BRUNHES and J. DUSSY (*Compt. rend.*, **118**, 1045—1046).—The viscosity of fused sulphur at first decreases, like that of other liquids, as the temperature rises. The rate of transpiration increases from the melting point to a point between 156—157°; it then diminishes very rapidly, and at 162° it has become so viscous that it cannot be forced through a tube 1 mm. in diameter, even by the pressure of a column of mercury 700 mm. high. At higher temperatures, a change in the opposite direction takes place, and may be regarded as a second fusion.

At 156°, the rate of transpiration of the sulphur is 1·796 that at 115·5°. The rate of transpiration at 115·5° is 0·0518 and at 156° 0·093 that of water at 25·5°. C. H. B.

Dissociation of Water. By W. NERNST (*Zeit. physikal. Chem.*, **14**, 155—156).—The author points out that, in the determination of the electrolytic dissociation of water by Ostwald (Abstr., 1893, ii, 365), the difference of potential between the acid and base employed must not be neglected. He calculates this to be about 0·065 volt, and hence finds the dissociation to be $0·8 \times 10^{-7}$. L. M. J.

Dissociation of Saline Hydrates and Analogous Compounds. By H. LESCŒUR (*Ann. Chim. Phys.* [7], **2**, 78—117).—A continuation of the author's previous experiments (Abstr., 1893, ii, 364). Determinations of the tension of dissociation of several chlorides, bromides, and iodides are given, and from these data, as well as, in some case, by direct analysis, the existence of the following hydrates is established. $MgCl_2 + 8H_2O$ (only obtained on one occasion; crystallises in long, silky fibres); $MgCl_2 + 6H_2O$; $MgCl_2 + 4H_2O$; $ZnCl_2 + 2H_2O$; $CdCl_2 + 4H_2O$; $CdCl_2 + H_2O$; $FeCl_2 + 6H_2O$; $FeCl_2 + 4H_2O$; $FeCl_2 + 2H_2O$; $FeCl_2 + H_2O$; $Fe_2Cl_6 + 12H_2O$ (yellow); $Fe_2Cl_6 + 8H_2O$ (red). The following peculiarity of the yellow hydrate, which has been noticed by Berzelius, is without parallel; thus, instead of efflorescing in the air, it deliquesces, losing its water. The existence of the hydrates to be mentioned was also established: $CuCl_2 + 3H_2O$; $CuCl_2 + 2H_2O$; $CuCl_2 + H_2O$. Cuprous chloride is anhydrous; when agitated with water, it is converted into cuprous

oxide, but the yellow substance, which Wöhler believed to be the intermediate oxychloride, is simply a mixture of cuprous chloride and cuprous oxide. $BaBr_2 + 2H_2O$; $BaBr_2 + H_2O$; $MgBr_2 + 6H_2O$; $MgBr_2 + H_2O$; $ZnBr_2 + H_2O$; $CdBr_2 + 4H_2O$; $MnBr_2 + 4H_2O$; $MnBr_2 + H_2O$; $FeBr_2 + 2H_2O$; $FeBr_2 + H_2O$; $Fe_2Br_6 + 6H_2O$; $Fe_2Br_6 + 3H_2O$; $NaI + 4H_2O$; $LiI + 6H_2O$; $BaI_2 + 6H_2O$; $MnI_2 + 6H_2O$; $MnI_2 + 4H_2O$; $MnI_2 + 2H_2O$; $MnI_2 + H_2O$; $FeI_2 + 2H_2O$; $FeI_2 + H_2O$. The lower hydrates are, in general, better defined by their tensions of dissociation than the higher hydrates; these latter, by successive dehydration, pass gradually into lower hydrates. The tension of dissociation alone is not, therefore, as Debray believed, sufficient to indicate the existence of a hydrate.

The following table shows the results obtained by saturating with hydrogen chloride a saturated solution of the chlorides; it would seem that only those aqueous solutions having a greater tension at 20° than 8·5 mm. are precipitated by hydrogen chloride.

Initial compound.		Product precipitated by HCl.	
Maximum tension of the saturated solution at 20°.	Tension of dissociation at 20°.		Tension of dissociation at 20°.
mm.	mm.		
$BaCl_2 + 2H_2O$ .. About 15·45	About 3	$BaCl_2 + H_2O$ ..	Very small.
KCl .... ,, 13·55	Nil	KCl	Nil.
NH_4Cl .... ,, 13·40	Nil	NH_4Cl	Nil.
NaCl .... ,, 13·10	Nil	NaCl	Nil.
$CdCl_2 + 4H_2O$ .. ,, 12·20	About 10·5	$CdCl_2 + H_2O$..	Below 2·0 mm.
$SrCl_2 + 6H_2O$... ,, 11·50	,, 5·6	$SrCl_2 + 2H_2O$.	1·8 .,
$CuCl_2 + 3H_2O$ .. ,, 9·80	,, ,,	$CuCl_2 + 2H_2O$, green	Below 2·0 ,,
$CoCl_2 + 6H_2O$... ,, 9·05	,, 4·0	$CoCl_2 + 2H_2O$, blue	Very small.
$NiCl_2 + 6H_2O$ .. ,, 8·60	,, 4·6	$NiCl_2 + 2H_2O$, yellow	,,
$FeCl_2 + 6H_2O$... ,, ,,	., ,,	$FeCl_2 + 4H_2O$, green	,,
$MnCl_2 + 4H_2O$ .. ,, 8·00	,, 3·8	$MnCl_2 + 2H_2O$, white	,,
$MgCl_2 + 8H_2O$.. ,, 10·90	,, ,,	$MgCl_2 + 4H_2O$	Below 2 mm.
$MgCl_2 + 6H_2O$.. ., 5·75	,, 1·8	No precipitate	,,
$Fe_2Cl_6 + 12H_2O$.. ,, 6·50	,, ,,	,,	
$CaCl_2 + 6H_2O$ .. ,. 5·40	,, 2·3	,,	
$ZnCl_2 + 2H_2O$ .. Below 2·00	,, ,,	,,	

A. R. L.

Rate of Diffusion of some Electrolytes in Alcohol. By W. KAWALKI (*Ann. Phys. Chem.*, [2], **52**, 300—327).—The results of the author's experiments on the rate of diffusion of electrolytes in alcohol

(this vol., ii, 308) are given in a series of tables, and the following conclusions are drawn from them.

The rate of diffusion increases as the concentration of the initial solution is diminished, the increase becoming more and more marked as the concentration decreases. With very small initial concentrations, the values calculated for the diffusion coefficient k from the determination of the concentrations of the different layers of the diffusate are not found to correspond with one another, although greater regularity is observed when the initial concentrations are high. This behaviour is probably due to convection currents in the dilute solutions, which disturb the regular course of the diffusion. The ratio of the diffusion coefficient in aqueous solution k' to that in alcoholic solution k is constant for any one salt, and practically independent of the concentration. It is also approximately equal to the ratio of the molecular conductivities for solutions of infinite dilution. as the following table of comparative values shows.

	k'/k.	$\lambda'_\infty/\lambda_\infty$.
NaI	2·72	2·62
LiCl.................	3·09	3·07
KOAc...............	2·52	2·92
NaOAc	2·31	2·50
KI	3·08	2·60
AgNO₃	3·12	3·00

From this it appears that the rate of motion of the ions in water is about three times greater than in alcohol. The absolute values of the ionic velocities cannot be calculated from the author's results, but comparative values are obtainable, which accord with conclusions drawn from the electrolytic dissociation theory.　　　　　H. C.

Absorption of Hydrogen by Water and Aqueous Solutions.

By P. STEINER (*Ann. Phys. Chem.*, [2], **52**, 275—299).—The author has determined the absorption coefficient of hydrogen by water and a number of aqueous solutions of different concentrations. For water at 15°, the value 0·01883 was obtained, and the values of the

$m =$	1.	2.	3.	4.	5.	6.
LiCl.................	1574	1325	1121	949	—	—
KNO₃...............	1524	1276	1076	—	—	—
AlCl₃	1511	1221	993	810	667	550
KCl	1502	1217	996	820	—	—
NaNO₃..............	1496	1201	984	808	667	542
CaCl₂...............	1493	1195	958	780	635	510
NaCl................	1478	1144	880	699	573	—
MgSO₄	1451	1120	856	659	499	—
ZnSO₄...............	1446	1113	852	667	510	—
Na₂SO₄..............	1370	991	710	—	—	—
K₂CO₃...............	1338	967	700	508	372	273
Na₂CO₃..............	1340	967	699	—	—	—
Cane sugar..........	1280	731	—	—	—	—

absorption coefficients for the solutions examined are given in the table.

In this table, m represents the number of gram-equivalents per litre of the solution, and the absorption coefficients have been multiplied by 10^5. The author also gives a table of the values of the equivalent depression of the absorption coefficient $\varphi = (0\cdot01883 - \beta)/m$, where β is the absorption coefficient of the solution of concentration m. Attention is called to the almost identical values obtained for $MgSO_4$ and $ZnSO_4$, and for K_2CO_3 and Na_2CO_3, the latter case being the more striking, as coincidence is not observed in the case of the other pairs of sodium and potassium salts examined.   H. C.

Physical Properties of Hydrated and Anhydrous Compounds.

By S. SURAWICZ (*Ber.*, **27**, 1306—1316).—The author shows, by a general comparison of a large number of anhydrous compounds with the same substances in the hydrated condition, that the anhydrous compounds crystallise in systems of higher symmetry than the hydrated. Thus, in the case of the chloride, bromide, and iodide of sodium, the anhydrous salt is cubic, but the salt crystallising with $2H_2O$ is, in each case, monoclinic. Hydration is attended, therefore, with a diminution in crystallographic symmetry, and a consequent considerable change in the thermal, optical, and many other chemical and physical properties. Among the latter may be reckoned a decrease in specific gravity and hardness, and an increase in specific volume, as comparison of anhydrous and hydrated compounds shows.

There are a certain number of exceptions to the above rule, some of which, however, are, as the author shows, only apparent. Cases of complete exception are $NaHSO_4$, triclinic, and $NaHSO_4 + H_2O$, monoclinic, and the bromo-derivatives of anhydroecgonine, which are monoclinic in the anhydrous, and tetragonal in the hydrated, state.

                                                          H. C.

Speed of Reduction of Ferric Chloride by Stannous Chloride.

By L. KAHLENBERG (*J. Amer. Chem. Soc.*, **16**, 314—323).—The well-known reaction between ferric and stannous chlorides proceeds slowly enough at zero to admit of study from the standpoint of chemical dynamics. By a series of carefully conducted experiments, the author has proved that the reaction follows the law of Guldberg and Waage fairly well.

In accordance with this law, the speed of the reduction of ferric chloride by an equivalent proportion of stannous chloride is expressed by the equation

$$\frac{dx}{dt} = c(a - x)^2,$$

in which a represents the amount of substance present at the outset, x the amount of substance changed during the time t, and c a constant depending on concentration, temperature, etc.

Free hydrochloric acid at first favours the reaction, but if more be added, the reaction is sensibly interfered with towards the end.

                                                    L. DE K.

Reaction-velocities. By J. E. TREVOR and F. L. KORTRIGHT (*Zeit. physikal. Chem.*, **14**, 149—150).—In the inversion of cane sugar by an acid, the molecular concentration increases, and there should, therefore, be a corresponding variation in the boiling point and other properties dependent on the molecular concentration. By observations, therefore, of the increase in the boiling point at various stages of the inversion, the reaction-velocity may be determined according to the equation $\frac{1}{t} \log \frac{z}{z-x} = ka$, where z is the total increase, x that after time t, and a the concentration of the hydrogen ions. Results for 13 observations extending over 85 minutes, when 90 per cent. of the sugar was inverted, gave results for k varying only to the extent of 3 per cent.   L. M. J.

New Method of Determining the Relative Affinities of certain acids. By M. C. LEA (*Amer. J. Sci.*, [3], **47**, 445—451).— A method of measuring affinities is described, which is based on the principle that the affinity of any acid is proportional to the amount of base which it can retain in the presence of a strong acid selected as a standard of comparison for all acids. Sulphuric acid is here taken as the standard, and its presence or absence in the free state is ascertained by means of the herapathite test (compare Abstr., 1893, ii, 566). If we suppose that the quantity taken is always a gram molecule at a fixed rate of dilution, it is evident that 2 gram mols. of sodium hydroxide would exactly saturate it. If we now take a given acid, we may find that a quantity of its sodium salt corresponding with 3 gram mols. of sodium hydroxide will exactly extinguish the reaction of a gram molecule of free sulphuric acid. With still another acid, we find that a quantity of its sodium salt corresponding with 4 gram mols. of sodium hydroxide is needed to extinguish the sulphuric acid reaction. Then the affinity of the second acid is exactly twice as great as that of the first. Thus in the case of hydrochloric acid, there was required 29·37 gram mols. of sodium chloride to extinguish the reaction in 1 gram mol. of sulphuric acid. The quantity 27·37 gram mols. is the proportion of undecomposed sodium chloride that must remain in the solution in order that the sulphuric acid, may be completely converted into sodium sulphate. This number 27·37, therefore, represents the strength of the affinity of hydrochloric acid for sodium. But in order to compare acids of different basicities, it is convenient to refer them all to bibasic sulphuric acid, and therefore the above number must be halved. Hence 13·68 may be taken as the index of the affinity of hydrochloric acid in comparison with those of other acids determined in like manner.

In this way the numbers given for the following acids were obtained: succinic, 0·21; acetic, 0·14; citric, 0·53; pyrophosphoric, 0·926; tungstic, 0·2. The applicability of the method was a good deal restricted owing to the tendency of many acids to decompose the herapathite reagent. Without obtaining exact numbers, it was, however, found that chloric acid has the strongest affinity for bases of any known acid, and that the comparative affinity of nitric acid

has hitherto been placed somewhat too high. Taking hydrochloric acid as 100, nitric acid scarcely exceeds 75. Qualitative experiments show that extremely feeble acids, such as hippuric and salicylic, are able to take a certain quantity of base, even from so strong an acid as sulphuric, setting free a recognisable quantity of the latter acid. Carbonic anhydride, however, even under pressure, does not liberate any portion of sulphuric acid from sodium sulphate.

In order to obtain true comparative results by the above method, it is necessary to use the sulphuric acid always at exactly the same dilution, and to add the dry salt to it. The affinity of sulphuric acid for water is, indeed, a most important factor in all determinations of this nature, as the following case illustrates. When 4 c.c. of normal sulphuric acid are added to 40 c.c. of normal sodium nitrate, not a trace of free sulphuric acid can be detected in the liquid. But when, instead of 4 c.c. of normal sulphuric acid, 40 c.c. of decinormal acid are used, although the quantities of acid and salt are exactly the same, the result is quite different, as free sulphuric acid then exists in the solution, and is abundantly indicated by the herapathite test.

<div align="right">H. C.</div>

Graphochemical Calculations. By E. NICKEL (*Zeit. physikal. Chem.*, **14**, 93—104).—An application of the author's methods to nitrogenous compounds of the general formula $C_nH_mN_p$ (compare Abstr., 1892, 1158 ; 1893, ii, 119 ; this vol., ii, 235). L. M. J.

Isomorphism. By J. W. RETGERS (*Zeit. physikal. Chem.*, **14**, 1—52, (compare Abst., 1891, 146, 1151 ; 1892, 1048 ; 1893, ii, 193 ; this vol., ii, 85).—Elements and simple inorganic compounds crystallise mostly in the regular and hexagonal systems, 85 per cent. of the elements, 88 per cent. of diatomic compounds, and 53 per cent. of triatomic compounds obeying this rule ; complex inorganic and organic compounds, on the other hand, form crystals belonging chiefly to the rhombic and monoclinic systems. The author points out that owing to this connection between crystallographic form and chemical simplicity, many compounds are only apparently and not really isomorphous, and contests the isomorphism of numerous compounds, such as lead, silver, and cuprous sulphides ; mercuric and cupric sulphides ; sulphides and arsenides or antimonides ; whilst the isomorphism of sulphur and tellurium is also regarded as doubtful. The influence of chemical simplicity, however, extends only to form and not to miscibility, which the author therefore regards as the test of isomorphism. The frequent agreement of the crystallographic forms of metals, and their oxides or sulphides is also due to this cause, and not to any peculiar influence of the metal. The author does not consider the coloration of crystals by aniline and other dyes to be analogous to the formation of mixed crystals, but rather to a phenomenon akin to capillarity—the absorption of the dyes into the intermolecular spaces. The paper concludes with a discussion of the probable constitution of the plagioclase felspars. L. M. J.

Fractional Precipitation. By T. PAUL (*Zeit. physikal. Chem.*, **14**, 105—123).—If a mineral acid is added to a saturated solution of

an organic salt, a quantity of the organic acid is formed, and may be precipitated, the quantity being calculable if the solubility and dissociation data are known. A number of such data obtained experimentally, are given, and then the results of experiments performed with single acids. In this case the quantity precipitated is given by the equation $(S - l - u)(H - l - u) = C$, where S is the number of the acid radicles, H the number of hydrogen atoms, l the undissociated acid, and u the number of molecules precipitated. The acids examined were orthiodobenzoic, cinnamic, and paratoluic, and in each case the agreement between observed and calculated results was very good. The author points out also that the method could be used in the converse way to determine the dissociation of the acid. In the case of a mixture of two acids, two equations are necessary. If both acids are precipitated, there are

$$(1.) \quad (S - l - u_1)(H - l_1 - u_1 - l_2 - u_2) = C_1$$
$$(2.) \quad (S - l - u_2)(H - l_1 - u_1 - l_2 - u_2) = C_2,$$

whilst if one acid alone is present to saturation and is precipitated, $u_1 = 0$, and $C_1 = k_1 l_1 v$. This second case is first examined in the cases of mixtures of metabromobenzoic and orthotoluic acids; orthiodobenzoic and cinnamic acids; and orthiodobenzoic and paratoluic acids, close agreement with calculated numbers being in each case obtained. For the experiments on the precipitation of both acids, a large number of mixtures of iodobenzoic, toluic, cinnamic, and anisic acids were employed; the results, although not as concordant as in the previous cases, were still satisfactory. It is possible, the author points out, by the proper addition of the mineral acid to almost completely separate the pure acids from a mixture of their salts.

<div align="right">L. M. J.</div>

Sedimentation and Dye-absorption. By O. LEHMANN (*Zeit. physikal. Chem.*, **14**, 157—160).—Many compounds if dissolved in a liquid containing finely suspended material induce a precipitation of the particles, whilst in the case of colouring materials the dyes may also be precipitated. The action of a large number of compounds in causing the deposition of the carbon in Indian ink is recorded, and the author considers that the effect appears to depend on the formation around the particle of a layer of the dissolved material, so that the weight of the particles becomes so great that they can no longer remain suspended. The effect of thickening the solution is to retard the sedimentation, and the effects in this direction of different compounds are given.

<div align="right">L. M. J.</div>

A Continuous Automatic Mercury Air-pump for Chemical Purposes. By G. W. A. KAHLBAUM (*Ber.*, **27**, 1386—1394).—For a detailed description and figure of the pump, reference must be made to the original paper. The pump consists of two parts: a Sprengel pump, and an apparatus in which the mercury that flows away from the Sprengel is sucked up by the current of air induced by a water-pump. It is thus sucked up in the form of short columns, separated by spaces of rarefied air, and as the total height of this composite column can be much greater than that of the barometer, it is possible

in this manner to raise the mercury to such a height that it will flow back into the top of the Sprengel for further use there. The modification of the pump described is intended for use in vacuum-distillation; the distillation-apparatus is evacuated as far as possible with the water-pump, and then the pressure is reduced to 1 mm. with the mercury-pump. This last diminution of pressure is very advantageous; for instance, whilst a reduction of pressure from 760 to 50 mm. only lowers the boiling point of benzyl alcohol by 80°, a reduction from 10 to 1 mm. lowers it by 32°.   C. F. B.

Inorganic Chemistry.

Reaction of Sulphur and of the Halogens with Normal Sodium Pyrophosphate. By T. SALZER (*Arch. Pharm.*, **231**, 663 —667).—Girard (*Compt. rend.*, **56**) stated that when sulphur is boiled with an aqueous solution of normal sodium pyrophosphate, orthophosphoric and thiosulphuric acids are formed. The author has studied the reaction between sulphur and normal sodium pyrophosphate in aqueous solution, and finds that no orthophosphoric acid is produced, but that the reaction occurs in the sense of the following equation, where x depends on concentration, temperature, and pressure :

$$x\mathrm{Na_4P_2O_7} + 12\mathrm{S} + 3\mathrm{H_2O} = 2\mathrm{Na_2S_5} + \mathrm{Na_2S_2O_3} + 6\mathrm{Na_3HP_2O_7} + (x - 6)\mathrm{Na_4P_2O_7}.$$
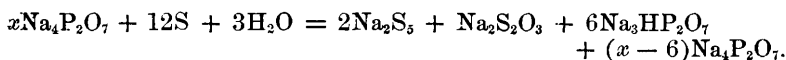
The halogens react with an aqueous solution of sodium pyrophosphate in a similar manner, the products being sodium bromide, sodium hypobromite, and trisodium hydrogen pyrophosphate, much normal sodium pyrophosphate being left unattacked.   A. G. B.

Action of Potassium Hydrogen Arsenite on the Salts of the Metals. By C. REICHARD (*Ber.*, **27**, 1019—1036).—The author has investigated the action of acid potassium arsenite, $\mathrm{K_2O,2As_2O_3,H_2O}$, on a number of metallic salts in dilute aqueous solutions. The following table exhibits the results obtained, the formulæ ascribed to the various arsenites having, in all cases, been established by analysis.

Composition.	Mode of preparation.	Properties.	Previous description.
$\mathrm{Hg_2O,As_2O_3}$ ..	From $\mathrm{HgNO_3}$	Yellowish mass, decomposing in light	Berzelius.†
$2\mathrm{CuO,As_2O_3}$ ..	,, $\mathrm{CuSO_4}$*.	Green powder.......	Bloxam.
$2\mathrm{CdO,As_2O_3}$ ..	., $\mathrm{CdSO_4}$*...........	White, non-crystalline powder	—
$2\mathrm{HgO,As_2O_3}$..	,, $\mathrm{HgCl_2}$*	Yellowish-white mass, decomposing in light	Berzelius.†

Composition.	Mode of preparation.	Properties.	Previous description.
$2PbO,As_2O_3$ ..	From $Pb(C_2H_3O_2)_2$*	White	PbO,As_2O_3 by Filhol† as being formed in this way.
$3Au_2O,As_2O_3$.	,, $AuCl_3$*	Purple-red powder; blackens when heated or exposed to light	—
$3Ag_2O,As_2O_3$.	,, $AgNO_3$*	Yellow microscopic needles; decomposes in light	Obtained by many authors.
$3PbO,As_2O_3$ ..	,, $2PbO,Pb(C_2H_3O_2)_2$.	White	Streng; Kühn.
$3MgO,As_2O_3$..	,, $MgSO_4$*	White powder	Stein.
$3ZnO,As_2O_3$ ..	,, $ZnSO_4$*..........	White crystalline mass	Bloxam.
$5SnO_2,2As_2O_3$.	,, $SnCl_4$*..........	Yellowish-white mass	Berzelius.†
$5TiO_2,2As_2O_3$.	,, $TiOSO_4$*	White crystalline substance	—
PtO_2,As_2O_3...	,, $PtCl_4$*..........	} Light yellow masses	{ Simon.†
PdO_2,As_2O_3...	,, $PdCl_4$*		—
UO_2,As_2O_3 ...	,, $UO_2(NO_3)_2$.......		—
Fe_2O_3,As_2O_3..	,, $FeCl_3$*...........	Rust-yellow powder..	—
Al_2O_3,As_2O_3 ..	,, $Al_2(SO_4)_3$*	White substance	Thorey.†
Cr_2O_3,As_2O_3 ..	,, $Cr_2(SO_4)_3$*	Dark green mass, soluble in KOH	—
FeO,As_2O_3 ...	,, $FeSO_4$............	Greenish-white substance; turns brown in the air	—
BaO,As_2O_3 ...	,, $Ba(NO_3)_2$.........	White substance, soluble in much water	—
$3CoO,2As_2O_3$.	,, $Co(NO_3)_2$*	Amethyst-coloured powder	} Girard.
$3NiO,2As_2O_3$.	,, $Ni(NO_3)_2$*	Light green substance	
$3CaO,2As_2O_3$.	,, $CaCl_2$*............	{ White powders, soluble in much water	—
$3SrO,2As_2O_3$..	,, $Sr(NO_3)_2$*		—
$3MnO,2As_2O_3$.	,, $MnCl_2$*...........	White, becoming pink to brown in the air	Stein.
$3SnO,2As_2O_3$..	,, $SnCl_2$*...........	Yellowish-white mass, decomposed by acids and alkalis with separation of free arsenic	Berzelius.†

* Indicates that the respective acids were set free during the formation of the new salt.

† In these cases the salts had not been analysed by the earlier investigator.

A. H.

Salts of Rubidium. By H. ERDMANN (*Arch. Pharm.*, **232**, 3—36).
—Chemically pure rubidium salts are best prepared by making use
of ferric rubidium alum, which can be obtained quite free from
potassium salts, since ferric potassium alum is not only very soluble
in water but has the property of dissociating in solution. The author
has prepared pure specimens of a large number of rubidium salts, and

has studied their physical properties, more particularly the density, refractive index, and solubility in water. The following compounds have been examined:—$RbHSO_4$; $Rb_2S_2O_7$; Rb_2SO_4; $RbAl(SO_4)_2 + 12H_2O$; $RbFe(SO_4)_2 + 12H_2O$; $RbCr(SO_4)_2 + 12H_2O$; $RbBF_4$; $Rb_3Co(NO_2)_6 + H_2O$; $RbMgCl_3 + 6H_2O$; $RbClO_4$; $RbClO_3$; $RbIO_3$; $RbHI_2O_6$; RbI; $RbICl_4$.

Rubidium alum melts at 105°; its refractive index is 1·45648 at 20—23°. The sp. gr. of ferric rubidium alum is 1·9520; $n = 1·48225$ at 21—22°, corresponding with the molecular refraction 135·63. For rubidium iodide $n = 1·6262$, the molecular refraction $= 38·45$ and the sp. gr. is 3·447.

Mercuric iodide dissolves in a solution of rubidium iodide, a yellow *double salt* being formed. When this salt is treated with water, mercuric iodide is set free, since its solution is stable only when excess of rubidium iodide is present. Rubidium iodotetrachloride (Wells and Wheeler, Abstr., 1893, ii, 68) is dissociated by heat into rubidium chloride and iodine trichloride; its solution liberates iodine from potassium iodide, and on adding ammonia to it, a black precipitate of iodide of nitrogen is at once formed. A concentrated solution of the salt attacks metals, dissolving even gold and platinum. The author concludes by discussing the physiological action of rubidium iodide, and its application in pharmacy. M. O. F.

Barium Nitride. By BERTHELOT and MATIGNON (*Ann. Chim. Phys.*, [7], **2**, 144).—*Barium nitride*, BaN_6, is obtained by treating a solution of ammonium nitride with an equivalent weight of barium hydroxide, and evaporating the solution under diminished pressure in the cold; it thus furnishes beautiful crystals. The gram-molecular heat of dissolution at 19·8° is —7·8 Cal. A. R. L.

Copper Bromide. By P. SABATIER (*Compt. rend.*, **118**, 980—983). —Dilute solutions of cupric bromide are blue, but when concentrated by evaporation at the ordinary temperature they become emerald green, then dark green, and finally red-brown, the solution depositing bulky, black, monoclinic prisms of the anhydrous bromide $CuBr_2$. This salt is highly deliquescent; heat of dissolution at 12° $= +7·9$ Cal., a value which agrees well with Thomsen's (8·2 Cal.).

In winter the brown solutions *sometimes* deposit long, brilliant, bottle-green, monoclinic needles of the hydrate $CuBr_2,4H_2O$. It is very deliquescent; heat of dissolution at 7·5° $= —1·5$ Cal.

It follows that—

$CuBr_2$ sol. $+ 4H_2O$ sol. $= CuBr_2, 4H_2O$ sol. develops $+ 3·7$ Cal.

Like hydrated metallic chlorides the heat of hydration of which is less than 2 Cal. per molecule of water, the hydrated cupric bromide effloresces in dry air, and loses all its water; its behaviour when freely exposed to the atmosphere depends on the degree of humidity of the latter. Dehydration takes place even in solution, the green liquid becoming temporarily brown and opaque when heated.

Alcohol dissolves the anhydrous bromide, forming highly opaque, yellowish-red solutions.

When a minute quantity of cupric bromide is added to concentrated

hydrobromic acid, an intense purple coloration is produced, in consequence, probably, of the formation of a hydrobromide of the bromide. This reaction is more sensitive than either the ferrocyanide or sulphide reaction, and will detect 0·0015 milligram of copper in a drop of a solution of the bromide, but the hydrobromic acid must be concentrated. A mixture of potassium bromide with a saturated solution of phosphoric acid can be used instead of hydrobromic acid.

C. H. B.

The Molecular State of Calomel Vapour. By W. HARRIS and V. MEYER (*Ber.*, **27**, 1482—1489).—After enumerating the experiments of previous observers, the authors describe some new ones which they have made. A sheet of gold leaf, dipped for a moment in calomel vapour, becomes amalgamated; if held there longer the coating of mercury evaporates. A thermometer immersed in rapidly evaporating calomel indicated 357°, a temperature very nearly that of boiling mercury. The rate of volatilisation of calomel at different temperatures was approximately determined, and the vapour density at 448° and at 518° was found, by V. Meyer's method, to correspond with the constitution HgCl, or Hg + HgCl$_2$. The same vapour density was obtained with a mixture, in these proportions, of mercury and corrosive sublimate, and, on cooling, calomel was deposited in the apparatus. When calomel, contained in a porous cell, was heated at 465° inside a test-tube, mercury vapour was found to have diffused through the porous walls, and condensed on the walls of the test-tube, while some mercuric chloride was found inside the porous cell. Further, if a rod of potash, previously heated to 240—260°, is dipped into the vapour of calomel at the same temperature, it is *immediately* covered with a yellow coat of mercuric oxide, whereas a black coat of mercurous oxide only begins to turn yellow at this temperature after the lapse of some 20 seconds. All these facts indicate that calomel as such is not volatile, but that its " vapour " is completely dissociated into mercury and mercuric chloride.

C. F. B.

Calomel. By E. DIVERS (*J. Soc. Chem. Ind.*, **13**, 108—111).—The author concludes from his experiments on a Japanese method of manufacturing a peculiar form of calomel that in this case the calomel is formed by a reaction between mercury vapour, oxygen, and hydrogen chloride gas, $4Hg + 4HCl + O_2 = 4HgCl + 2H_2O$, and that the reaction takes place at a temperature near to the boiling point of mercury, and much below that at which calomel volatilises. The calomel cannot be the result of true sublimation, but of precipitation as fast as it is formed from the three gaseous substances which give rise to it, and its not reaching its subliming temperature is the explanation of its freedom from corrosive sublimate.

L. T. T.

Crystallisation of Gold in Hexagonal Forms. By A. LIVERSIDGE (*Chem. News*, **69**, 172—173).—When precipitating a solution containing 15 grains of sodium aurochloride, $AuCl_3,NaCl,2H_2O$, to 15 ozs. of water, by means of freshly fractured fragments (i) of copper pyrites, (ii) of the graphitic casing from an auriferous vein, or (iii) of zinc blende, the gold was observed to be deposited in very small, bril-

liant, lustrous prisms arranged in fan-like groups, or in six-rayed stellate tufts, or in some instances in the form of minute hexagonal plates. Many sulphides precipitate the gold as an ochre-coloured, lustreless, mammillated film, whilst cubical crystals are obtained by precipitation with ferrous sulphate, oxalic acid, &c. This is, however, as the author points out, not the first time that hexagonal crystals of gold have been observed.   D. A. L.

Mineralogical Chemistry.

Condition of Gold in Quartz and Calcite Veins. By A.
LIVERSIDGE (*Chem. News*, **69**, 162—163).—Removing gangue and
associated minerals by chemical means—hæmatite, spathic iron, and
calcite by hydrochloric acid; mispickel, &c., by nitric acid, or by
roasting and subsequent treatment with hydrochloric acid; quartz,
&c., by hydrofluoric acid—enabled the author to examine the condi-
tion of the residual gold. Generally, the gold from hard matrices
like quartz is found to be non-crystalline, but occurs as irregular
films, plates, threads, or masses more or less connected together, and
when the gangue is dissolved away forms a spongy or cavernous mass;
such gold has been obtained from Mount Morgan stalactitic hæmatite,
from New Caledonia Reef (Queensland) quartz, and from many other
specimens of gold quartz; on the other hand, crystalline gold is en-
countered in the weathered and decomposed parts of quartz reefs, in
what are now cavities, and in soft matrices such as the gold-bearing
calcites of the New South Wales gold mines and the Gympie mines
of Queensland, the serpentine of Gundagai, and Lucknow, and some
of the clear quartz from New Zealand. The larger the fragments of
gold, the less the tendency to crystalline form. The author has also
observed crystalline form in alluvial gold from Fairfield, New Eng-
land, N. S. W., it was not water-worn, and so had not travelled far
from the parent reef. D. A. L.

Gold Ores of California. By H. W. TURNER (*Amer. J. Sci.*, [3],
47, 467—473).—As is well known, gold in California occurs chiefly in
quartz veins, usually in the slate series of the Sierra Nevada. It
occurs, however, in a great variety of rocks, and associated with
very different minerals. The occurrences grouped geologically are
enumerated by the author, those cited being veins in the auriferous
slate series, and veins in the granite. He instances the occurrence
of gold in albite, in calcite with barytes and with cinnabar, and in
rhyolite with quartz. B. H. B.

Artificial Zinc Oxide and Wurtzite. By H. TRAUBE (*Jahrb. f.
Min. Beilage*, **9**, 147—153).—1. Zinc oxide as a metallurgical pro-
duct has frequently been described. The author has, however, col-
lected at the smelting works in Upper Silesia some well-developed

crystals of zinc oxide of unusual form and colour. The crystals described are colourless, yellow, green, and dark brown. The axial ratio is considerably affected by the presence of small quantities of foreign elements, as is shown by the following table.

Colour.	Composition.	$a : c.$
Colourless...............	Pure	1 : 1·60770
Yellow	Traces of CdO, FeO	1 : 1·60317
Green	0·38 FeO, traces MnO	1 : 1·66835
Brown..................	0·48 FeO, 0·27 MnO, traces CdO	1 : 1·64026

2. Wurtzite as a metallurgical product has been described by Förstner and by Stahl. The author has found this substance in very large quantities in the lead slags of the Friedrichs works at Tarnowitz. Its composition was found to be as follows.

Fe.	Zn.	Mn.	Pb.	S.	Total.
0 81	66·02	trace	trace	32·79	99·62

B. H. B.

Composition of Wavellites and Turquoises. By A. CARNOT (*Compt. rend.*, **118**, 995—998).—Four specimens of wavellite had the following composition, the fluorine being determined by the author's method (Abstr., 1892, 911).

	F.	P_2O_5.	Al_2O_3.	Fe_2O_3.	CaO and MgO.	H_2O.	Clay and quartz.	Total.
A.	1·90	32 38	37·03	0·40	traces	27·72	0·43	99·86
B.	2·79	33·40	37·44	0·64 (FeO)	traces	26·45	—	100·72
C.	2·09	33·55	36·83	0·36	traces	27·53	0·16	99·86
D.	1·81	22 07	34·82	1·40	traces	26·16	3·75	100·01

A, from Cork, Ireland, was in greyish mamelons, and dull grey radiating fibres ; B, from Clonmel, Ireland, was similar in structure, but yellowish-green and dull green in colour; C, from Chester, U.S.A., was in small, white, elongated stalactites ; and D, from Garland, Arkansas, was in greyish, globular masses, composed of radiating fibres. The mean of the four analyses is

P_2O_5.	Al_2O_3.	F.	H_2O.
33·20	37·38	2·17	27·25

which corresponds with the formula $2(Al_2O_3,P_2O_5) + Al_2(O_3,Fl_6) + 13H_2O$.

Two specimens of oriental turquoise, one (E) from Persia, and the other (F) from Nevada had the following composition.

	P_2O_5.	Al_2O_3.	FeO.	MnO.	CuO.	CaO.	Clay.	H_2O.
E.	29·43	42·17	4·50	—	5·10	—	0·21	18·59
F.	30 38	44·82	5·32	0·22	7·40	traces	—	11·86

Fluorine is absent.   The composition of the mineral corresponds only very approximately with the formula $P_2O_5,(Al_2,Cu_3,Fe_3)O_3 + Al_2O_3 + 5H_2O$.

Two specimens of occidental turquoise or odontolite had the following composition : G, from Munster, Ireland, was greenish-blue, whilst H had the same colour but was uniform in tint.

F.	P_2O_5.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	CO_2.	Clay.	Loss on heating.
G. 3·02	43·46	22·59	6·45	20·10	traces	5·07	0·37	—
H. 3·45	41·27	17·71	5·80	24·72	0·99	5·60	0·18	1·20

Odontolite is not constant in composition, which is a natural result of the fact that it is an alteration product formed under a variety of conditions.   C. H. B.

Analysis of Pele's Hair from Hawaii.   By A. H. PHILLIPS (*Amer. J. Sci.*, [3], **47**, 473—474).—The author gives the following results of analyses of Pele's hair (I) and of a stalagmite (II) from the lava caves of Kilauea.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	P_2O_5.	CaO.	MgO.
I.	50·76	14·75	2·89	9·85	0·41	0·26	11·05	6·54
II.	51·77	15·66	8·46	6·54	0·82	—	9·56	4·95

	Na_2O.	K_2O.	Total.
I.	2·70	0·88	100·09
II.	2·17	0·96	100·89

B. H. B.

Beaver Creek Meteorite.   By E. E. HOWELL, W. F. HILLE-BRAND, and G. P. MERRILL (*Amer. J. Sci.*, [3], **47**, 430—435).—This meteorite fell between 3 and 4 P.M., May 26, 1893, near Beaver Creek, West Kootenai District, British Columbia.   It is a typical aerolite of very pronounced chondritic structure with the usual fused black crust.   Its unusual feature is that beneath the crust there is a slight oxidation for a distance of $\frac{1}{2}$ in. to $\frac{3}{4}$ in.   Analysis shows the meteorite to be composed of 17·13 per cent. of nickel iron, 0·16 per cent. of magnetite, 5·05 per cent. of troilite, 37·23 per cent. of soluble silicates and phosphate, and 40·43 per cent. of insoluble silicates and chromite.   B. H. B.

Physiological Chemistry.

Acid in Protozoan Digestion. By M. GREENWOOD and E. R. SAUNDERS (*J. Physiol.*, **16**, 441—467).—The secretion of acid by protozoa as determined by litmus and alizarin sulphate has been mooted by other observers, especially by le Dautec.

In the experiments now recorded, acid indicators were admin-

istered in combination with food stuffs. The infusorian, *Carchesium polypinum*, and the plasmodia of certain mycetozoa were selected as subjects for the experiments. In the method of ingestion, the formation of vacuoles, and the exclusive digestion of proteïds, the phenomena observed were closely similar to those previously recorded in rhizopods.

The ingestion of solid matter of whatever nature always stimulates the cell to secrete an acid fluid round it in a more or less extensive vacuole. This acid is, however, not a digestant, but delays digestion. The process of digestion is accompanied by a gradual and finally total disappearance of the acid.

From its behaviour to congo-red, the acid is judged to be free acid, and not carbonic acid. W. D. H.

Influence of Ferments occurring in Vegetables on the Nutrition of the Organism. By H. WEISKE (*Zeit. physiol. Chem.*, **19**, 282—284; compare this vol., ii, 286).—In certain vegetables, amylolytic, proteolytic, and other ferments occur. In order to prove whether these assist digestion in the animal organism, or at least increase the nutritive value of the food, rabbits were during one period fed on the raw vegetable (oats) ; and during another on the oats which had been heated to destroy the ferments. The intake and output of material were measured in the usual way, and the results were practically the same during both periods.

W. D. H.

Red Blood Corpuscles of different Specific Oxygen Capacities. By J. H. HALDANE and J. L. SMITH (*J. Physiol.*, **16**, 468—475). —In relation to Bohr's work on this subject, it is here recorded that there are distinct differences, amounting sometimes to more than 20 per cent., in the specific oxygen capacity of different layers of corpuscles in centrifugalised blood. But no relationship was found constant between this capacity and the layer, or the size, or specific gravity of the corpuscles. W. D. H.

Ground Substance of Connective Tissue. By R. A. YOUNG (*J. Physiol.*, **16**, 325—350).—The forms of connective tissue investigated were those that contain but few formed elements (cells and fibres), and a large amount of ground substance or matrix. The general results obtained may be briefly summarised as follows :—

1. The vitreous humour is extremely poor in solids containing only slightly over 1 per cent. ; the intact vitreous shows a great resistance to the action of digestive juices or putrefaction.

2. The vitreous humour contains mucin, although in comparatively small quantities and very possibly as mucinogen. It has the reactions of a typical mucin, except that it is distinctly soluble in excess of acetic acid.

3. From the so-called membranes of the vitreous, distinct, although small, quantities of gelatin can be obtained.

4. The vitreous contains two other proteïds, namely, a globulin coagulating at 75°, and an albumin coagulating about 80°.

5. Whartonian jelly yields large quantities of mucin in two forms,

one soluble, the other insoluble, in excess of acetic acid. This mucin is acid in reaction, and darkens on exposure.

6. It also yields two proteïds, one like myosin coagulating at 56°, and an albumin coagulating at 84°.

7. The reducing product or gummose obtained from funis mucin reduces Fehling's, but not Barfoed's reagent. It gives a brown, amorphous compound with phenylhydrazine, and yields no catechol on being heated with strong alkali.

8. Funis mucin is not digested by artificial gastric juice, but is readily digested by artificial pancreatic juice, and the products (mucin-albumose and peptone) yield, like the mucin from which they come, a reducing substance on heating with dilute mineral acid.

W. D. H.

Chemistry of Muscle. By A. WHITFIELD (*J. Physiol.*, 16, 487—490).—Myosin is a globulin, not a nucleo-albumin. It contains an appreciable amount of phosphorus in its molecule; on gastric digestion, it leaves only an insignificant residue, and this contains no phosphorus. It does not produce intravascular coagulation.

Muscle contains no nucleo-albumin. Proteoses (albumoses) and peptone are also absent.

W. D. H.

Bone in Osteomalacia. By M. LEVY (*Zeit. physiol. Chem.*, 19, 239—270).—The mineral constituents are less in the bones of osteomalacial patients than in normal bones. The relation $6PO_4 : 10Ca$ of normal bone ash remains the same in osteomalacia. The diminution in the phosphate, therefore, proceeds *pari passu* with that of the carbonate.

Fresh normal bones treated with lactic acid lose much more carbonate than phosphate. Osteomalacia cannot, therefore, be explained by the presence of lactic or other free acid.

The organic constituents of the bone show in this disease no qualitative change. But the relative increase of marrow leads to an increase in the proportion of proteïd to gelatin.

W. D. H.

Development of Heat in Salivary Glands. By W. M. BAYLISS and L. HILL (*J. Physiol.*, 16, 351—359).—From the experiments recorded, the conclusion is drawn that no development of heat can be directly determined in the submaxillary gland by any known method of measuring variations in temperature.

W. D. H.

Formation of Glycogen. By J. FRENTZEL (*Pflüger's Archiv.*, 56, 273—288).—Cremer states that pentoses increase the quantity of glycogen in the liver, not because they are themselves transformed into glycogen, but because they exercise a sparing influence.

The present research relates to the same question. It was found that by the use of strychnine, animals can be rendered glycogen-free. On giving xylose, it was found that no glycogen was subsequently discoverable.

Control experiments showed that glycogen was formed if other substances were administered that ordinarily give rise to glycogen either directly or by a sparing action.

W. D. H.

Formation of Urea in the Liver. By C. RICHET (*Compt. rend.*, 118, 1125—1128).—The liver continues to exhibit after its removal from the body, while the vitality of its cells lasts, the same chemical phenomena as while it is within the body. For instance, sugar is formed from its glycogen. The present research shows that the same is true for the formation of urea, and the opinion is advanced that this, like the formation of sugar, is due to a ferment action. W. D. H.

Diastatic Ferment of the Liver. By E. SALKOWSKI (*Pflüger's Archiv.*, 56, 351—354).—It is pointed out that the use of chloroform water, which destroys protoplasm but leaves enzymes intact, has been employed by the author previous to the appearance of Bial's paper (this vol., ii, 106). The result of this work coincides with that of Bial, that the conversion of glycogen into sugar is the result of a diastatic ferment action. W. D. H.

Ferment Processes in Organs. By H. SCHWIENING (*Virchow's Archiv.*, 136, 444—481).—In this communication a number of questions are taken up, the link connecting the various researches together being Salkowski's observation that chloroform water destroys living protoplasm and formed ferments, but is inactive on enzymes. Here, then, is a means of distinguishing in an organ undergoing changes after its removal from the body whether or not an enzyme is the cause of the change.

An organ is taken, divided into two parts, one of which (A) is subjected to the action of chloroform water, the other (B) boiled and sterilised; both are examined after the lapse of a certain time. In A the xanthine substances go completely, in B incompletely, into solution. If a liver is examined, A contains sugar, no glycogen, large quantities of leucine and tyrosine; it does not give the biuret reaction. In B there are only traces of sugar, abundant glycogen, and no leucine or tyrosine; it gives the biuret reaction. The acidity in the two cases is the same, but the amount of organic substances, nitrogen, and phosphoric anhydride that go into solution are greater in A than in B.

In the case of muscle, A gives no biuret reaction, but a weak reduction of Fehling's solution; whilst B gives a biuret reaction, but no reduction. In A the acidity is increased. In both, leucine and tyrosine are absent; there is no rise in the soluble organic substance, nitrogen, or phosphoric anhydride, as in the liver.

These results of Salkowski's are extended in the present paper, and the ferment action is termed auto-digestion.

The formation of sarcolactic acid after death is regarded as a vital phenomenon. The muscle forms acid not because it is dead or dying, but because it is still alive.

Experiments with chloroform water lend no support to the theory that the liver forms sugar from glycogen in virtue of the vital activity of its cells, but the presence of a ferment is considered necessary. Curiously enough, boiling does not inhibit the change of glycogen into sugar. This has been observed before, and the explanation con-

sidered most feasible is that the ferment is destroyed by heat, but that fresh ferment appears as the disintegration of the cells subsequently takes place.   W. D. H.

Influence of Decomposition of Proteïd on the Output of Neutral Sulphur. By N. SAVELIEFF (*Virchow's Archiv.*, **136**, 195—202).—An experiment relating to proteïd metabolism was made on a dog. The intake in nitrogen was the same every day, but during four days in the middle of the research 200 c.c. of chloroform water was given with the food. This led to an increased output of nitrogen, and also of sulphur, in which the proportion of neutral sulphur to the total sulphur in the urine was increased.   W. D. H.

Analyses of Milk. By J. LEHMANN and W. HEMPEL (*Pflüger's Archiv.*, **56**, 558—578).—The analyses relate chiefly to the ash associated with caseïn. The caseïn of cow's milk contains 7·2 per cent. of ash : this consists of CaO, 49·5 ; MgO, 2·4 ; P_2O_5, 47·0 ; and SO_3, 1·06 per cent. The elementary composition of caseïn is thus given : C, 50·86 ; H, 6·72 ; N, 14·63 ; P, 0·81 ; S, 0·72 ; ash, 6·47 per cent. The caseïn of woman's milk contains more sulphur (1·09 per cent.) and less ash (3·2 per cent.). The composition of milk is given thus :—

	Cows' milk.	Human milk.
Caseïn	3·0	1·2
Albumin	0·3	0·5
Fat	3·5	3·8
Lactose	4·5	6·0
Ash	0·7	0·2
Water	88·0	88·5

W. D. H.

Influence of Cold Baths on the Excretion of Nitrogen and Uric acid. By E. FORMÁNEK (*Zeit. physiol. Chem.*, **19**, 271—281).—Cold baths naturally call on the organism for an increased production of heat, and the present research, carried out on human beings, shows that the increased metabolism falls in part on the proteïds of the body. A single bath-day makes little or no difference, but a succession of these raises the total output of nitrogen slightly, and of uric acid very slightly. The average of 24 days which were normal or bathless gives *per diem* total output of nitrogen 14·88, and of uric acid 0·7025 grams. The average of seven days, on which two cold baths were taken, gives 15·46 and 0·7194 respectively.   W. D. H.

Carbonic Oxide Poisoning. By G. MARTHEN (*Virchow's Archiv.*, **136**, 535—547).—Five cases of poisoning by carbonic oxide are given, with clinical details. In all, the body temperature was elevated. As regards metabolism, the decomposition of proteïd is enormously increased. There may be slight albuminuria. The pulse is like that of typhoid fever. The red corpuscles of the blood are increased considerably.   W. D. H.

Action of Oxalates on Nerve and Muscle. By W. H. HOWELL (*J. Physiol.*, **16**, 476—486).—Irrigation of a nerve in frogs and terrapins by dilute solutions of sodium oxalate destroys its irritability towards electrical stimuli, without, however, killing it, as a well-marked demarcation current is present ; which, however, more rapidly disappears than in normal nerve.

In a nerve muscle preparation, it is the motor end plates which are first affected. The suggestion is made that removal of calcium salts will explain the loss of irritability.

The loss of irritability in muscle is preceded by convulsive twitchings, and, contrary to the observations of Cavazanni, the oxalated muscle went in every case into *rigor mortis* sooner than a normal muscle. W. D. H.

Arrow Poisons. By L. LEWIN (*Virchow's Archiv.*, **136**, 82—126, 403—443).—This is a historical account of the subject of arrow poisons, together with some physiological experiments on animals, relating to their action ; in some cases the source of the poison is given or guessed at ; the question of the chemical substances present is hardly gone into, and in no case completely. The account of the different poisons used by various and numerous tribes shows that they vary considerably. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Formation of Resins and Ethereal Oils in Plants. By A. TSCHIRCH (*Ann. Agron.*, **20**, 299—300; from *Jahrb. Wiss. Bot.*, **25**, 370; *Bot. Centr.*, **57**, 18).—The following products were examined. Sumatra and Siam benzoïn (*Styrax benzoin*), Peru balsam (*Myroxylon pereiræ*), Tolu balsam, styrax (*Liquidambar orientalis*) and galbanum (*Ferula galbaniflua, rubicaulis*, &c.). When hydrolysed, they yield, on the one hand, aromatic (chiefly benzoic and cinnamic) acids, or alcohols, and a group of "resin alcohols" or "resinols," on the other. *Benzoresinol*, $C_{16}H_{26}O_2$; *resinotannol*, $C_{18}H_{20}O_4$; *siaresinotannol*, $C_{12}H_{14}O_3$; *peruresinotannol*, $C_{18}H_{20}O_5$; *storesinol*, $C_{12}H_{19}O$; and *galbaresinotannol*, $C_6H_{10}O$, were obtained. The termination "tannol," signifies that the alcohols give the tannin reaction. Resin alcohols yield with aromatic acids, or with other alcohols, ethers which seem to be identical with the natural ethereal salts of resins.

Resins frequently contain free acids and alcohols, as well as ethers. The fact that the highly carbonaceous resins and essences are formed at the earliest period of the life of the plant, when all disposable matter is utilised in the building up of new tissues, would seem to indicate that these compounds have an important biological *rôle*. N. H. M.

Composition of the Cotton Plant. By Hutchinson and Patterson (*Bied. Centr.*, 1894, 403—404).—The analyses of the plants were made at six stages of growth, and the first set were undertaken in 1890, when the plants grew on a dark grey loam overlying close clay; whilst in 1891 the soil was a porous, yellow loam; the main difference in the composition of the soils is to be found in the potash and lime, K_2O 0·540, CaO 0·255, in 1890, and K_2O 0·34, CaO 0·145, in 1891, but the ash constituents are vastly different.

1890.

	Crude protein.	Fat.	Carbohydrates.	Fibre.	Ash.	SiO_2.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	P_2O_5.	SO_3.
Roots........	6·39	2·92	38·76	48·59	3·34	5·32	3·47	16·08	11·00	23·28	2·38	10·05	3·31
Stem........	6·71	2·24	33·04	54·93	3·06	1·80	0·63	20·36	11·31	24·80	4·08	9·53	3·62
Leaves......	21·62	7·84	41·52	14·49	14·53	3·13	0·90	35·66	7·86	12·60	1·64	9·31	6·71
Seed........	21·09	9·67	29·83	33·73	5·68	2·01	1·50	10·10	8·15	37·92	4·04	19·25	6·81

1891.

	Crude protein.	Fat.	Carbohydrates.	Fibre.	Ash.	SiO_2.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	P_2O_5.	SO_3.
Roots........	3·25	2·50	37·78	52·54	3·93	28·47	8·34	11·91	7·43	20·07	3·86	13·83	2·21
Stem........	6·95	1·79	39·45	47·45	4·36	5·58	4·01	21·09	5·46	26·61	4·68	12·74	3·23
Leaves......	18·60	9·86	49·06	10·56	11·92	4·16	2·20	34·22	7·64	15·99	2·08	14·38	8·16
Seeds......	11·84	3·19	66·42	14·74	3·81	3·34	7·22	10·63	10·06	35·55	0·68	20·40	7·59

E. W. P.

Seeds of " Chenopodium album L." By G. BAUMERT and K. HALPERN (*Arch. Pharm.*, **231**, 641—644).—These seeds are sometimes used as a substitute for rye. It will be seen from the following tables that, although the seeds are richer in nitrogenous matter and fat than is either rye or wheat, they contain a smaller total of digestible constituents. In rye or wheat flour the chenopodium betrays itself by its high content of ash and fibre.

Composition of Seeds of Chenopodium album L.

	Baumert and Halpern.		Erismann.	Kapustin.	Salmenew.	Mean.
	Seed.	Husk (Calyx leaves).				
	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Water	10·33	7·45	10·66	17·04	10·92	12·22
Nitrogenous matter*	13·94	12·25	13·88	15·75	17·60	15·29
Fat	6·97	2·86	6·28	5·88	6·93	6·51
Nitrogen-free extract	39·30	39·66	47·42	37·70	38·52	40·73
Fibre	25·68	17·93	16·52	17·58	21·45	20·31
Ash	3·88	19·85	5·24	6·05	4·58	4·94
*Containing proteïds	12·56	9·91	—	—	—	—

Mean composition of	Water.	Ash.	Fibre.	Fat.	Nitrogenous matter.	N-free extract.
Wheat (König) ..	13·65	1·81	2·53	1·75	12·35	67·91
Rye (König)	15·06	1·81	2·01	1·79	11·52	67·81
Chenopodium ...	12·22	4·94	20·31	6·51	15·29	40·73

A. G. B.

Cacao Bean. By H. BECKURTS (*Arch. Pharm.*, **231**, 687—694). —The author gives a detailed account of the methods adopted for estimating the fat, theobromine, and starch in the cacao bean. The variations from the usual methods are in details alone, and can only be appreciated by reference to the original. Tables are given which show the analytical data obtained from 23 trade brands. The following table gives the maxima and minima of these data.

	Per cent.
Fat*	42·00—57·40
Theobromine	0·63— 2·20
Starch	7·56—16·53
Ash	2·20— 3·75

* Chloroform extract, freed from dissolved theobromine by treatment with water.

Constants of fat :—

Melting point...................	30·0—36·5°
Melting point of fatty acids	48·5—53·0°
" Saponification number "	193—220
Iodine absorption...............	32·8—40·0

<div align="right">A. G. B.</div>

Henbane Seed Oil. By H. SCHWANERT *(Arch. Pharm.,* **232,** 130—136).—This oil consists chiefly of oleïn, with a small quantity of palmitin and traces of colouring matter; it is free from alkaloïds. The iodine number by Gantter's process is 64·48, the Hübl method giving 156·25. The author attributes this discrepancy to the employment of mercuric chloride in the latter process.   M. O. F.

Manuring with Phosphates, &c. By MÄRCKER *(Bied. Centr.,* 1894, 374—376).—The researches have extended over three years, and have been chiefly directed to the examination of the action of phosphates. It is an error to believe that the "after action" of a phosphatic manuring continues for so long, or is so intense as is generally supposed ; and it is found that even in those soils richest in phosphates, the third crop begins to shrink in quantity.

With basic slag, the same amount of straw may be obtained as when superphosphate is used, but the yield of grain is far less, even to one-half as little, and doubling the amount of slag does not double the crop of grain ; likewise in its after action basic slag is behind superphosphate. Bones only act well on soils already containing a fair supply of phosphates.   E. W. P.

Analytical Chemistry.

Estimation of Oxygen in the Blood. By I. Novi (*Pflüger's Archiv*, **56**, 289—303).—Siegfried (*Archiv. Anat. Physiol. Physiol. Abth.*, 1890, 385) states that blood only gives up a part of its oxygen to sodium hyposulphite; more can be extracted by the air pump. The blood which has lost this portion of oxygen shows no trace of oxyhæmoglobin bands with the spectroscope, that which remains is in a compound called pseudohæmoglobin. The apparatus used by Siegfried has been modified by Schützenberger, and some more alterations are suggested in the present paper. The experiments recorded confirm Siegfried's main contention, but show that the amount of oxygen removable by his method varies considerably in different animals, and in the same animals under different conditions.   W. D. H.

Estimation of the Strength of Sulphuric acid. By H. D. Richmond (*Chem. News*, **69**, 236).—The author has made a careful determination of the density of mixtures of weighed quantities of sulphuric acid and water, the results point to the correctness of a

table prepared from Pickering's results (Trans., 1890, 64 *et seq.*), Lunge and Isler's table (Abstr., 1891, 150) being found to be quite wrong. D. A. L.

Estimation of Phosphorus in Iron, Steel, and Ores containing Arsenic. By J. O. HANDY (*J. Amer. Chem. Soc.*, **16**, 231—234).—The author has found that when testing iron by the molybdate process, the yellow, phosphatic precipitate nearly always contains more or less arsenic, although in the absence of phosphorus no precipitate is obtained at all. The precipitate may be freed from arsenic by dissolving it in 15 c.c. of dilute ammonia (1—6), diluting with water to 75 c.c., and, after heating to 75°, adding a mixture of 10 c.c. of nitric acid (sp. gr. 1·42) and 25 c.c. of Wood's molybdate solution. It is then washed with dilute nitric acid (1—100), dried, and weighed, or else titrated, as usual. L. DE K.

Dudley's Method of estimating Phosphorus in Steel. By O. S. DOOLITTLE and A. EAVENSON (*J. Amer. Chem. Soc.*, **16**, 234—247).—The authors have, by a special process, reinvestigated the nature of the yellow phosphomolybdate precipitate, and confirmed the usually accepted statement that the ratio between phosphorus and molybdic acid must be taken as 1·792.

The means adopted for reducing the molybdic acid have a considerable influence on the results of the titrating process. The reduction should be carried out by dissolving the precipitate in dilute ammonia, adding granulated zinc and shot, and then boiling with excess of dilute sulphuric acid.

The authors also find that there is little danger of arsenic precipitating with the phosphorus if the iron solution is not heated above 32°. L. DE K.

Comparison of Pemberton's Method of Estimating Phosphoric acid with the American Official Process. By W. C. DAY and A. P. BRYANT (*J. Amer. Chem. Soc.*, **16**, 282—283).—The agreement between the two methods is remarkably close. There is no exaggeration in Pemberton's statement, that a sample of phosphate may be analysed in some 30—40 minutes. L. DE K.

Direct Estimation of Citrate Soluble Phosphoric acid. By B. B. ROSS (*J. Amer. Chem. Soc.*, **16**, 304—308).—Citric acid interferes with the precipitation of phosphoric acid with molybdate solution, and several devices have been proposed to remove it from the phosphatic solution. The author now recommends destroying it by immitating Kjehldahl's method, and operates as follows. After digesting the phosphate with 100 c.c. of the official citrate solution, 25 c.c. of the liquid is at once filtered into a dry vessel, preferably a burette, and, after cooling, an aliquot part is put into a digestion flask of 250—300 c.c. capacity, 15 c.c. of strong sulphuric acid is added, and the flask put on a piece of gauze over a moderately brisk flame. After about 8 minutes, foaming and darkening will set in; after further lapse of 3—4 minutes the foaming will cease. About 1 gram

of mercury is now added, and the digestion continued over a high flame; after about half an hour, a clear and almost colourless liquid will be obtained.

The solution is washed into a beaker, rendered slightly alkaline with ammonia, then acidified with nitric acid, and treated by the regular molybdate method. The test analyses are entirely satisfactory.   L. DE K.

Recovery of Molybdic acid from Residues, and Remarks on Phosphoric acid Estimation. By H. BORNTRÄGER (*Zeit. anal. Chem.*, **33**, 341—343).—The whole of the filtrates, both acid and ammoniacal, from the phosphoric acid precipitates, are poured into a large flask containing ammonia. Pure molybdic acid separates in fine needles. The liquid is finally made nearly neutral, the precipitate collected on a filter, washed slightly, and pressed. It is then dissolved in the least possible quantity of ammonia, the solution rapidly filtered from silica and magnesia, diluted with water to a density of 1·11, and poured into an equal volume of nitric acid of 1·2 sp. gr., allowed to deposit for 24 hours, and the clear solution poured off for use.

The author, with Fresenius, adds fuming nitric acid to the ammoniacal solution of the yellow precipitate, until the precipitate produced no longer dissolves immediately. The magnesia mixture is added to the hot solution, and filtration commenced as soon as air bubbles rise from the pulverulent precipitate, which takes place in 1—2 hours. The precipitate is incinerated without removal from the filter, and Barthel's spirit lamp is strongly recommended for the purpose.
                                                          M. J. S.

Estimation of Silica. By A. CAMERON (*Chem. News*, **69**, 171—172).—The author fused a sample of silica, containing 98·5 per cent. SiO_2, 0·1 of Fe_2O_3, 0·5 of Al_2O_3, 0·7 CaO, and 0·2 MgO, with fusion mixture decomposed with hydrochloric acid, evaporated to dryness in a porcelain basin, continuing the heating after the acid fumes were driven off, and then proceeded in the usual way, subsequently subjecting the filtrate to various treatments, including evaporating to dryness over a water bath and over a flame, with various strengths of sulphuric acid, or with hydrochloric acid, or in the presence of iron, of alumina, of calcium carbonate, or of organic matter. He finds that in all cases at least two evaporations are required to obtain all the silica from solution; that it is more effectually separated over the flame than over the water bath; that hydrochloric acid is as efficient as, and preferable to, sulphuric acid; that the admixtures make very slight difference to the purity of the silica, which was tested by treatment with hydrofluoric acid; and that repeated evaporations in the first instance show no advantage over the single evaporation.   D. A. L.

Estimation of Impurities in Commercial Nickel. By T. FLEITMANN (*Zeit. anal. Chem.*, **33**, 335—338).—The most usual impurities are iron, copper, cobalt, zinc, and manganese. Not less than 5 grams of the metal is dissolved in aqua regia, and the solution

repeatedly evaporated with hydrochloric acid. From the filtered solution the iron is precipitated by cautious neutralisation with dilute sodium carbonate, addition of a drop of acetic acid and boiling. The precipitate is again dissolved and thrown down by ammonia, when any copper it may have contained will be separated. To the filtrate from the iron precipitate, a drop of hydrochloric acid is added, and then saturated hydrogen sulphide solution drop by drop until the copper is exactly precipitated. Then by passing hydrogen sulphide gas through the filtrate, the zinc is precipitated as sulphide, which is subsequently converted into carbonate. The filtrate is freed from hydrogen sulphide by boiling, and after neutralisation by sodium carbonate is treated at 60—80° with feebly alkaline sodium hypochlorite. The manganese comes down first as brown manganic oxide, then the cobalt as blackish-brown cobaltic hydroxide, and then a small portion of the nickel as deep black nickelic hydroxide, the commencement of the precipitation of the latter being indicated by the evolution of oxygen. The liquid is boiled and the precipitate collected, dissolved from the filter with hot hydrochloric acid, the solution heated to expel chlorine, the hydrochloric acid replaced by acetic acid, and the cobalt and nickel precipitated by hydrogen sulphide and separated by potassium nitrite, which can very well be accomplished when the proportion of nickel is first reduced as above. The manganese is found in the filtrate as acetate. Traces of arsenic, antimony, and tin would be found with the iron precipitate ; lead with the copper. M. J. S.

Oxidation and Chemical Properties of Gases. By F. C. Phillips (*Amer. Chem. J.*, **16**, 340—365 ; compare this vol., ii, 293, 294).—Acetylene forms the well-known metallic compounds. The soluble silver compound constitutes the most delicate test, and is also the best means of preserving acetylene, the copper compound being liable to oxidation. Acetylene is oxidised to carbonic anhydride at the ordinary temperature by osmic acid, calcium hypobromite, or a solution of potassium permanganate in concentrated sulphuric acid, and by iodic acid at 90°. The osmic acid is reduced to metallic osmium, the iodic acid to iodine ; gold chloride is also reduced to metallic gold, and ferric chloride to ferrous chloride.

Allylene forms similar metallic compounds. The palladium compound is dark-brown, the silver compound white, the cuprous compound canary-yellow. Allylene is oxidised to carbonic anhydride by the same reagents as acetylene, and reduces gold and palladium to the metallic state. Unlike acetylene it does not precipitate ammoniacal silver nitrate. The formation of the silver compound constitutes the most delicate test.

Carbon oxysulphide may be separated and distinguished from hydrogen sulphide by means of dry mercuric oxide, copper carbonate, litharge or white lead spread on cotton-wool, with which substances it does not react. It reacts with solutions of metallic salts, the metallic sulphide and carbonic anhydride being formed. It is readily oxidised to carbonic anhydride and sulphuric acid by bromine water or acid permanganate.

Methylmercaptan may be separated from hydrogen sulphide by means of mercuric oxide, with which it combines only slowly. It forms compounds with many metals, mostly of different colour to the corresponding sulphides. The lead, copper, and silver compounds are yellow, the cadmium compound white. The metallic compounds are decomposed by hydrogen sulphide. Methylmercaptan is very stable towards oxidising agents. It is not oxidised even by a fused mixture of sodium carbonate and potassium dichromate or nitrate.

Methylic sulphide can be purified from hydrogen sulphide and methylmercaptan by means of an aqueous sodium hydroxide solution of lead hydroxide. The mercaptan may be recovered by heating the lead compound with dilute acid. The metallic compounds are all fairly soluble. Methylic sulphide is quite as stable towards oxidising agents as the mercaptan, and may be distinguished from the latter by means of the sparingly soluble palladium compound, which crystallises in microscopic, monoclinic prisms, and, unlike the corresponding compound from methylmercaptan, is readily soluble in hot water.

Nitrogen forms compounds with magnesium, lithium, and potassium.

Oxygen may be conveniently recognised in coal-gas and the like by passing the gas successively through caustic soda and manganous chloride solutions in closed vessels. When the air has been expelled, some of the soda is transferred to the manganese vessel. If oxygen is present, the resulting manganous hydroxide is oxidised to the brown hydrated peroxide. The test may be rendered still more delicate by the subsequent addition of potassium iodide and dilute sulphuric acid. Aqueous pyrogallol may be substituted for the manganous chloride.   JN. W.

Estimation of Glycerol in Wine. By H. D. PAXTON (*Chem. News*, **69**, 235—236).—10 c.c. of wine is treated with slaked lime, transferred drop by drop to an expanded piece of filter paper, dried at the ordinary temperature, extracted with absolute alcohol in a Soxhlet apparatus, the extract evaporated in a flask, redissolved in ether alcohol, filtered, evaporated, and the residue dried and weighed. There is less loss of glycerol than when other methods of evaporation are employed, whilst the glycerol appears to be quite as pure.

                                                                    D. A. L.

Butter Fat. By A. PIZZI (*Staz. Sper. Agrar.*, **25**, 101—118; compare this vol., ii, 75).—The following method was employed for fractionating the glycerides of butter by slow cooling. The butter (400 grams) was melted in a long tube, 8 cm. in diameter, placed in a thermostat kept at 80°. In about an hour, the melted butter was stirred with a glass rod and left for half an hour; it was then filtered through a hot filter into a weighed beaker. The amount of fat obtained in the experiment recorded was 234·89 grams. The beaker was now covered and placed in the bath heated at 80°; after 4 hours the gas was turned out and the whole left for two days, by which time the butter had cooled to the ordinary temperature of the laboratory (26·2°) and was partly solid. The liquid portion was removed by

filtration and finally by placing the solid substance on tiles. Two experiments made in 1891 and 1892 gave the following percentage results :—

	Solid glycerides.	Liquid glycerides.
1891	35·20	64·80
1892	32 90	67·10

Butter fat was further fractionated by cooling down to different temperatures and separating the solid matter each time. The temperatures employed were (1) 26·2°, (2) 21·2°, (3) 17·0°, (4) 12·4°, (5) 11·0° and (6) 6·5°. A table is given showing the sp. gr. of the liquid portion at each temperature, the melting and solidifying points of the solid matter, the volatile acids (as c.c. N/10 alkali) and the iodine numbers of both solid and liquid matter. As regards density, there is an increase as the temperature at which the separation was made decreases. The melting points decrease from 44° (solid separated at 26·2°) to 10·5° (solids separated at 6·5°), the melting point of the original being 36°. The volatile acids increased from 28 05 to 34·10 in the liquid, and from 19·91 to 31·02 in the solid portion. The iodine numbers also show a great increase. On comparing the amounts of volatile acids of the liquid fat of different periods, the results show a very regular difference between each period (except the period 4—3). Thus, the difference in amounts in periods 2 and 1 is 1·76; in 3 and 2, 1·76; in 5 and 4, 1·98; and in 6 and 5, 1·76.

The solid fat which separated at 26·2°, when magnified 170 diameters was seen to consist of globules without particular interest. It did not show any colours with polarised light. The solids obtained at 21·2—12·4°, consisted of little globules, whilst the fat which separated at 11—6·5 consisted of cruciform rosettes which showed in a remarkable degree the Newtonian colours. N. H. M.

Estimation of Fat in Bread. By M. WEIBULL (*Zeit. angw. Chem.*, 1895, 199—202).—The author's process (Abstr., 1893, ii, 197) having been tried, unsuccessfully, by Polenske, a large number of fresh experiments are communicated, showing the method to be perfectly trustworthy, but it is necessary to work exactly as follows :—

4 grams of new, or 3 grams of stale bread is put into a 70 c.c. beaker and covered with 30 c.c. of water, and 10 drops of dilute sulphuric acid. The whole is boiled, very carefully at first, over a very small straight flame for at least ¾ hour, some hot water being occasionally added to rinse the sides of the beaker. Towards the end the liquid is evaporated to about half its bulk. While still warm, the contents are carefully neutralised with powdered marble, a large excess being avoided. The mixture is then spread over a piece of filter paper (such as is used in Adam's milk process) and any liquid remaining in the beaker is removed by means of a piece of cotton-wool which is then put on to the filter paper. The latter, resting on iron gauze, is first dried for 10 minutes at 100°. The paper is now rolled into the usual shape, and then dried for 3—4 hours at 100—103°. After this it is placed in a Soxhlet's apparatus and

extracted at least 60 times with pure ether; this will generally take between four and five hours.   L. DE K.

A New Method of Analysing Fats and Resins. By P. C. McIlhiney (*J. Amer. Chem. Soc.*, **16**, 275—278).—The author's process is based on the fact that the unsaturated constituents of fats combine with bromine forming simple additive products, whilst resins and rosin oils are acted on with formation of hydrogen bromide.

The following reagents are required :—N/3 solution of bromine in carbon tetrachloride; N/10 solution of sodium thiosulphate; N/10 solution of potassium hydroxide. Not more than 1 gram of the sample of suspected oil is dissolved in 10 c.c. of carbon tetrachloride in a bottle of 500 c.c. capacity provided with a carefully-ground glass stopper. An accurately-measured excess of the bromine solution is added, the bottle tightly stoppered and placed in a dark place for 18 hours. The bottle is cooled with ice to form a partial vacuum, and a piece of wide rubber tubing, about 1½ inch long, is slipped over the lip of the bottle so as to form a well about the stopper. This well is filled with water and the stopper carefully lifted when the water will be sucked into the bottle and dissolve any hydrobromic acid. When 25 c.c. of water has been added, the bottle is well shaken and 20 c.c. of a 20 per cent. solution of potassium iodide is added. The liberated iodine is now estimated with thiosulphate, a check experiment being made as usual, and the difference is calculated to the percentage of bromine. The contents of the bottle are now transferred to a separating funnel, and the aqueous portion is separated, filtered through a cloth filter, and titrated with potassium hydroxide with methyl-orange as indicator. This gives the acidity which may be conveniently expressed in percentages of free bromine. Multiplied by 2 and deducted from the *total* bromine the bromine *addition* number is obtained.

The latter is *nil* for rosin and rosin oils, but reaches the high figures of 102·88 and 103·92 for fresh and boiled linseed oils. The author is engaged in the investigation of a large number of oils and resins by means of this method, and hopes to furnish new analytical *data* for their commercial analysis.   L. DE K.

Acetone in Urine. By E. Salkowski (*Pflüger's Archiv.*, **56**, 339—348).—In estmating acetone in urine by conversion into iodoform, the possibility that acetone might in part originate from carbohydrates in the urine during distillation was suggested. On putting this to the test of experiment, it was found that sugar in urine does give rise to a substance which gives many of the reactions of acetone, but which is an aldehyde, probably acetaldehyde.
W. D. H.

Chenopodine. Detection of Chenopodium Seed in Flours. By G. Baumert and K. Halpern (*Arch. Pharm.*, **231**, 648—653).— The evidence as to the injurious property of chenopodium is conflicting, and the existence of an alkaloïd in the plant has been disputed. Engelhard claimed to have isolated an alkaloïd from chenopodium

which he termed chenopodine. Reinsch sought to show that this base was identical with leucine. The authors find that both their predecessors were dealing with betaine, and the name chenopodine must therefore be expunged from chemical literature. Since betaine is not poisonous, the toxic action which chenopodium seed undoubtedly exerts in "Hungerbrot" must be attributed to some other constituent; neither a saponin compound nor oxalic acid is present, but there is a small quantity of an ethereal oil in the seed which has not been physiologically tested. Paracholesterol was detected in the ether extract of the seed. The rose or deep red colour which an alcoholic hydrochloric acid extract, made by some hours' digestion of chenopodium flour at a temperature somewhat above the normal, exhibits may serve for microscopical detection of the seed (compare this vol., ii, 363). A. G. B.

The Decomposition of Proteïds, &c., by Alkaline Hydroxides. By V. VEDRÖDI (*Zeit. anal. Chem.*, **33**, 338—340).—From the observation that tobacco freed from nicotine yields ammonia when distilled with soda (Abstr., 1893, ii, 504), the author was induced to attempt the estimation of the nitrogen in proteïds, etc., by this reaction, but in 12 hours' distillation, albumin, caseïn, glutin, and gelatin had yielded only 77, 60, 44, and 76 per cent. respectively of their total nitrogen. M. J. S.

The Analysis of Malt. By J. A. MILLER (*J. Amer. Chem. Soc.*, **16**, 353—360).—The author, having tried several methods, thinks the following process is the best. 50 grams of the sample is put into a weighed copper beaker, and mixed with 200 c.c. of water at 40°, which temperature is gradually increased to 60°. After 20 minutes' digestion, a few drops of the liquid is tested for starch, and should this be present the temperature is raised 1° every two minutes until it has completely disappeared. After cooling, water is added to make 450 grams total contents. After thoroughly mixing, the mass is thrown upon a plaited filter, but the first half of the filtrate is thrown back once more upon the filter. After collecting as much as possible of the filtrate, its sp. gr. is taken by means of the Westphal balance. From this gravity the percentage given by Schultze's tables is ascertained, and that number multiplied by 8·75, which gives the percentage of dry extract from the malt.

The author has experimentally proved that the extract cannot be accurately determined by evaporation and drying at 105° owing to the serious decomposition of maltose at that temperature. This, of course, applies to the estimation of extract in beers. Drying the extract at 70—75° is impracticable, except for scientific purposes. L. DE K.

Quantitative Separation of the Amorphous Nitrogenous Organic Compounds in Beer Wort. By H. SCHJERNING (*Zeit. anal. Chem.*, **33**, 263—299).—The precipitate produced by soda solution in beer wort contains a small proportion of the total nitrogen, that by baryta or stannous chloride a larger proportion, that by lead acetate still more, a further increase with ferric acetate, and the

largest amount with phosphomolybdic acid or uranium acetate. For all these reagents the author has investigated the conditions for the maximum precipitation, as well as the corrections for solubility in the filtrate and wash-waters. The substance precipitable by soda is also completely thrown down by baryta, phosphomolybdic acid, and uranium acetate, but not by the other reagents. The absolute baryta precipitate (the substance precipitable by baryta after that by soda has been removed) is identical with the stannous chloride precipitate, and is also precipitable by lead acetate, ferric acetate, phosphomolybdic acid, and uranium acetate. The lead acetate precipitate is also completely precipitable by ferric acetate, phosphomolybdic acid, and uranium acetate. The ferric acetate precipitate is completely thrown down by phosphomolybdic acid and uranium acetate. The phosphomolybdic acid precipitate contains all the constituents precipitable by the other reagents, together with all the ammonia in the wort. The uranium acetate precipitate contains the same nitrogenous constituents as the phosphomolybdic, with the exception of such of the ammonia as is not thrown down by the soda. The nitrogen in the soda precipitate is entirely in the form of ammonium magnesium phosphate, accompanied by other magnesium and calcium phosphates, magnesium saccharate, and traces of a lactate. Only about one-fourth of the ammonia in the wort is contained in this precipitate. The examination of the precipitates by the other reagents is, as yet, incomplete, but the absolute baryta precipitate seems to be an acid product of the splitting up of diastase, analogous to nucleïn, and for which the provisional name "Denucleïn" is suggested; the absolute lead precipitate seems to contain either unaltered mucedin or an acid albumin, the absolute ferric acetate precipitate to contain a propeptone, and that with uranium or phosphomolybdic acid actual peptones. A partial confirmation of this view results from the agreement of the sum of the lead and ferric acetate precipitates with that obtained by saturating the wort with magnesium sulphate.

M. J. S.

Peptone in Urine. By E. SALKOWSKI (*Chem. Centr.*, 1894, i, 658; from *Centr. Med. Wiss.*, 1894, 113—115).—Addition of commercial peptone to the extent of more than 0·01 per cent. to urine can be detected as follows :—50 c.c. of urine is acidified with 5 c.c. of hydrochloric acid, and precipitated with phosphotungstic acid and warmed. The precipitate, which aggregates on standing, is collected in a filter, washed twice with water, and then mixed with 8 c.c. of water and 0·5 c.c. of sodium hydroxide solution, by which means a deep blue coloration is developed. By warming in a test-tube, this becomes a dirty grey-yellow, and then on the addition of a few drops of a 1 per cent. solution of copper sulphate gives the usual biuret reaction. Urine rich in mucin, or albumin, must be freed from these in the usual way before applying the test.   W. D. H.

General and Physical Chemistry.

Line Spectrum of Oxygen. By B. HASSELBERG (*Ann. Phys. Chem.* [2], **52**, 758—761).—The author refers to the measurements of the line spectrum of oxygen by Eisig (this vol., ii, 265), criticises their accuracy, and draws attention to similar measurements made by Neovius (*Bih. K. Sven. Vet. Akad. Handl.*, 1891). H. C.

Absorption Spectra of Solutions of Cupric Bromide in Hydrobromic acid. By P. SABATIER (*Compt. rend.*, **118**, 1144—1146).—A solution of cupric bromide in hydrobromic acid, containing only 0·5 gram of copper per litre, is almost opaque (compare this vol., ii, 304), and the absorption spectrum can only be observed with very thin layers or in much more dilute solutions. With a freshly-prepared solution of 0·150 gram of copper in 780 grams of hydrobromic acid the transmission of light is distinct in the red, decreases rapidly in the yellow and green, shows a very distinct minimum in the blue at about λ 503, and then increases towards the more refrangible end. The colour of the solution is purple. A table is given showing the absorption coefficients, for various wave-lengths, of a solution of cupric bromide in hydrobromic acid, an alcoholic solution of the anhydrous bromide, and green and blue aqueous solutions. With wave-lengths shorter than λ 660, the coefficient is very high.

Even when protected from light, the solutions, after a little time, contain free bromine, the quantity of which increases rapidly with an increase in the quantity of cupric bromide, but is not proportional to it, the proportions of free bromine per litre after several months being 0·880 gram, 5·120 grams, and 6·08 grams, for 0·0255 gram, 0·175 gram, and 1·2 gram of copper. The hydrobromic acid is probably oxidised in presence of the cupric bromide in the same manner as hydrochloric acid in presence of certain chlorides. C. H. B.

Potential of Hydrogen and some Metals. By B. NEUMANN (*Zeit. physikal. Chem.*, **14**, 193—230).—Voltaic elements were formed consisting of the chain, mercury, potassium chloride, a normal salt solution, metal present in the salt. From the observations of the E.M.F, the difference of potential between the metal and its normal salt solution is calculable. For hydrogen salts, the electrode consisted of a platinum rod covered with a layer of platinum black, half immersed in the acid and half in hydrogen. A capillary electrometer was used, and the observations lead to the following results for the D.P. between the metal and solution (see next page).

It was also found that, as suspected, the last nine metals are precipitated from their solutions by hydrogen. Experiments with thallium salts indicated that, with equal concentration of the metallic ions, the negative ion has no influence on the Diff. Potential. The E.M.F.'s of chains containing various oxidisers and reducers were also

	Sulphate.	Chloride.	Nitrate.	Acetate.
Magnesium.........	+1·239	+1·231	+1·060	+1·240
Aluminium......	1·040	1·015	0·775	—
Manganese......	0·815	0·824	0·560	—
Zinc	0·524	0·503	0·473	0·522
Cadmium.......	0·162	0·174	0·122	—
Thallium........	0·114	0·151	0·112	—
Iron (ferrous) ...	0·093	0·087	—	——
Cobalt	−0·019	−0·015	−0·078	−0·004
Nickel	0·022	0·020	0·060	—
Tin	—	0·085	—	—
Lead	—	0·095	—	—
Hydrogen	0·238	0·249	—	0·150
Bismuth........	0·490	0·315	0·500	—
Antimony.......	—	0·376	—	—
Arsenic	—	0·550	—	——
Copper	0·515	—	0·615	0·580
Mercury........	0·980	—	1·028	—
Silver..........	0·974	—	1·055	0·991
Palladium	—	1·066	—	—
Platinum	—	1·140	—	—
Gold...........	—	1·356	—	—

observed, and hence the E.M.F. between the platinum and the oxidiser (*vel.* reducer). Of the 40 compounds examined, four only gave a + difference of potential, namely, stannous chloride, sodium sulphide, hydroxylamine, and chromous acetate. L. M. J.

The Solution Tension of Metals. By H. C. JONES (*Zeit. physikal. Chem.*, **14**, 346—360).—The author has determined the E.M.F. of voltaic chains in which the electrodes are silver, and the liquids solutions of silver nitrate of equal concentration in different solvents. One solvent was in all cases water, the others being ethylic alcohol, methylic alcohol, and acetone; in all cases, the water solution was negative to the other, the E.M.F. being 0·0956 for the ethylic alcohol chain, and 0·0906 for methylic alcohol, in both cases $N/10$ solutions, and 0·1512 with acetone ($N/100$). In the case of the ethylic alcohol chain, it is possible to calculate the ratio of the solution tension of the metal in the two solutions, using the equation E.M.F. $= 0·058$ ($\log p_1/P_1 - \log p_2/P_2$) where p_1 and p_2 are the osmotic pressures of the silver ions and P_1 and P_2 the solution tension of the silver in the two solutions, and hence results $P_1/P_2 = 0·024$. In the other cases examined, data for the dissociation of the silver salt are unavailable. The observations, however, certainly indicate that the tension of metals in different solvents is not constant, but is dependent on the nature of the latter. L. M. J.

Dielectric Constants and Chemical Constitution. By C. B. THWING (*Zeit. physikal. Chem.*, **14**, 286—300).—The author determines the dielectric constant of a number of solid and liquid substances by a method dependent on the resonance of electric vibrations. Details of the method are given in the paper, and the values of K for

a large number of liquid compounds. Researches are also recorded on mixtures of water with methylic and ethylic alcohols, glycerol, and acetic acid, curves embodying the results being given. In the case of the two alcohols the curve is almost a straight line joining the values of the two compounds, but in the aqueous mixtures singular points occur at compositions corresponding with definite hydrates, for instance, $C_2H_6O + 6H_2O, + 3H_2O, + H_2O$; $CH_4O + 4H_2O, + 2H_2O, + 1\frac{1}{2}H_2O$; $C_3H_8O_3 + H_2O$; $C_2H_4O_2 + 2H_2O, + H_2O$. The temperature variation of the dielectric constant of water was also investigated. The observed results are well reproduced by the use of the following atomic and group values, although in some cases the differences are far beyond experimental errors.

$$H = 2\cdot6 \qquad OH = 1356 \qquad CH_2 = 41\cdot6$$
$$C = 2\cdot6 \times 12 \qquad CO = 1520 \qquad CH_3 = 46\cdot8$$
$$O = 2\cdot6 \times 16 \qquad COH = 970 \qquad S = 2\cdot6 \times 16$$
$$X = 2\cdot6 \times M_x \qquad NO_2 = 3090$$

In the case of hydrocarbons and a large number of solids remarkable agreement is obtained by the use of the value $K = 2\cdot6$ D, where D is the density of the substance.   L. M. J.

Pure Water. By F. KOHLRAUSCH and A. HEYDWEILLER (*Zeit. physikal. Chem.*, **14**, 317—330).—The electrical conductivity of water in as high a state of purity as possible was determined, and that of pure water calculated from the results. The water was distilled and examined in a vacuum, as contact with air rapidly raises the conductivity, which, in some experiments, rose from $0\cdot11$ to $0\cdot14$ in four minutes, reaching $0\cdot58$ in two hours. The results at various temperatures of the purest water obtainable were

0°.	18°.	25°.	34°.	50°.
0·014	0·040	0·058	0·089	0·176

The value $\dfrac{dk}{dt}$ was calculated at various temperatures, and also the theoretical value as derived from the data of the dissociation theory, and from the result is deduced the value $k = 0\cdot0361$ for pure water at 18°, the difference $= 0\cdot0043$ being ascribed to impurities. The values for the dissociation of water derived from these experiments then became

	0°.	2°.	10°.	18°.	26°.	34°.	42°.	50°.
$10^{10}\alpha$ ...	0·36	0·40	0·57	0·80	1·10	1·45	1·91	2·44

L. M. J.

Electrical Conductivity of Feebly-dissociated Compounds and the Kohlrausch Method. By M. WILDERMANN (*Zeit. physikal. Chem.*, **14**, 231—246).—The author gives an account of the details of experiments on the conductivity of dichloracetic, trichloracetic, and β-resorcylic acids in absolute alcohol, all of which were carried out by Kohlrausch's method. The results of the experiments for varying dilutions are recorded, and the values for μ_{v_1}/μ_v compared with $\sqrt{v_1}/\sqrt{v}$, the law of dilution being obeyed to 18° by trichloracetic acid. The order of the dissociation of acetic acid and its chloro-

30—2

derivatives is the same in alcohol as in water, but the resorcylic acid does not occupy the position that would be expected from its aqueous dissociation. Kohlrausch's method is, however, unsuitable for slightly dissociated compounds, and almost useless for organic bases or acids in alcohol or other organic solvent, whilst even when applicable to such cases it is extremely tedious and troublesome.   L. M. J.

A new Method for Determining the Electric Conductivity of Feebly-dissociated Compounds. By M. WILDERMANN (*Zeit. physikal. Chem.*, **14**, 247—271).—The author had previously pointed out that Kohlrausch's method is inapplicable to feebly-dissociated compounds (preceding abstract), and describes a method which, for such cases, is more satisfactory. The chief difference lies in the use of a far stronger E.M.F., by which the polarisation becomes practically negligible, and a galvanometer can be employed instead of the telephone ; whilst also as the external resistances are very great, the measurement of the conductivity resolves into the measurement of the current, this being always done comparatively. The E.M.F. used was about 140—150 volts, obtained by 100 Clarke's elements, and the liquids were contained in capillary tubes of varying length and diameter. The results obtained for oxalic and acetic acids in aqueous solution are compared with those obtained by Kohlrausch's method, the agreement being entirely satisfactory. Experiments are then recorded in the case of dichloracetic acid and trichloracetic acid in alcoholic solution at various dilutions, and the molecular conductivity for the latter calculated, the results being $\mu_v = 0\cdot4294$ ($v = 1\cdot947$), and $\mu_v = 5\cdot343$ ($v = 996\cdot9$). It follows that trichloracetic acid in alcohol obeys the dilution law up to 25°.   L. M. J.

Dissociation in Solution. By A. SCHLAMP (*Zeit. physikal. Chem.*, **14**, 272—285).—The degree of dissociation of a number of salts in aqueous solution was determined by the elevation of the boiling point, and from the results the value M/M_a, the ratio of the molecular weight to the apparent molecular weight in its solution. This ratio is compared with that obtained by the conductivity or other methods, and the agreement appears satisfactory, except in the case of calcium chloride. When solvents other than water are employed, however, the different methods do not give such concordant numbers, as is seen from the following table.

Salt dissolved in propyl alcohol.	M/M_a from conductivity.	M/M_a from boiling point.
Lithium chloride	1·44	1·18
Sodium iodide	1·34	1·04
Calcium chloride	1·33	—
Lithium salicylate	1·17	0·55
Salicylic acid	1·00	1·05

<div align="right">L. M. J.</div>

Colour of Salts in Solution. By J. H. KASTLE (*Amer. Chem. J.*, **16**, 326—340).—The dissociation theory alone seems incompetent to explain the following facts concerning the colour of certain salts in solution.

1. The solutions of different salts of the same metal may and do possess two or more distinct colours.

2. The colour of salt solutions, in the cold, grows lighter, or is less, on dilution.

The hydrate theory of solution also seems incapable of satisfactorily explaining the facts. For example, it is difficult to conceive how the mere addition of water of hydration should work so radical a change in the properties of a compound as to change a white substance to one which is blue or red.

In view of the fact that the two theories mentioned above do not satisfactorily account for many of the observed facts, the author advances the hypothesis that the colour of a salt solution is dependent not on the colour of the ion, but on the colour of the base or that of the acid, either or both of which may be coloured; and, further, that the base or the acid to which the colour is due may possess, according to conditions at present unknown, two or more distinct colours. The argument is largely one of analogy. It has been proven, in the case of ferric salts, that at least two soluble, colloidal modifications of the hydroxide of iron exist, one brown, the other yellow; and, whilst ferric salts, in much of their conduct, offer an extreme case, it is assumed that the differences between them and other salts are of degree rather than of kind. Hence, if two soluble hydroxides of iron have been isolated, there may be yet another of this element and two or more of any other metal whose salts are coloured.

The following facts may also be cited in support of the view that we really have the free acid and base in solutions of coloured salts.

1. Most of these salts, if not all, are acid in reaction.

2. Most of them form basic salts readily.

3. Water in many of its reactions may be regarded as an acid, and hence the formation of hydroxides in solution is similar to double decompositions.

4. The many phenomena of the coloration of salt solutions, and the changes they sometimes undergo, which, as the author shows, are accounted for by this hypothesis.   H. C.

Solubility of Iodine in Carbon Bisulphide: Nature of Solution. By H. Arctowski (*Zeit. anorg. Chem.*, **6**, 392—410; compare this vol., ii, 308).—The author has determined the solubility of iodine in carbon bisulphide at a series of temperatures lying between —94° and +42°; the method used consists in saturating carbon bisulphide with iodine at the required temperature, then transferring a part of the solution to a tared flask containing mercury and again weighing. The carbon bisulphide is then evaporated off in a vacuum and the residual mercuric iodide and mercury weighed; the weight of both iodine and carbon bisulphide is thus determined. The solubility at low temperatures was determined by cooling a fairly strong solution by means of solid carbonic anhydride and ether, or some convenient cooling agent, filtering off the deposited iodine, and analysing the solution as above.

The solubility curve lying between the above limits of temperature

is composed of six straight lines connected together by short curved pieces. The author uses his results to support his previously expressed views respecting the nature of solution.   W. J. P.

Solubility of Ethylic Ether. By J. SCHUNCKE (*Zeit. physikal. Chem.*, **14**, 331—345).—The mean of a number of experiments gave the following results for the ether absorbed by 1 gram of water,

0°........	0·12465	20°........	0·07487
10	0·09599	30	0·06370

and for the water absorbed by 1 gram of ether,

10°........	0·02702	20°........	0·02720

The solubility of hydrogen chloride in ethylic ether was also determined, the analyses yielding the following values for the weight of the gas in 1 gram of the solution:—

—9·2°.....	0·3751	14·8°......	0 2780
+0·4	0·35407	30	0·1947

The solubility of ether in aqueous solutions of hydrogen chloride at six concentrations, varying from 3·65 to 31·61 per cent., was also determined, and the results recorded in both tabular form and by curves, a table being finally given also for the specific gravity of the acid at different temperatures.   L. M. J.

Affinity Constants of Weak Acids and the Hydrolysis of Salts. By R. W. WOOD (*Amer. Chem. J.*, **16**, 313—325).—In a preliminary paper (this vol., ii, 83) the author described a method for determining the apparent action of salts on the affinity constants of weak acids. A weighed amount of diastase is allowed to act for a given length of time, at a given temperature, on a weighed amount of starch, in the presence of known amounts of acids or salts. The action of the diastase is inhibited by acids or alkalis, and by determining the amount of sugar formed in each case the retarding power is measured. The numerical results published in the first paper are of qualitative value only, for it has since been found that slight variations in temperature, not sufficiently guarded against in the earlier work, had a far greater influence than was supposed, a change of half a degree in temperature being sometimes equivalent to a change of 10 per cent., or more, in the amount of the acid. A method of operating under conditions favourable for maintaining a constant temperature has, therefore, been devised, and is described in the paper.

The action of the fatty acids on diastase was first tried, with a view of determining the affinity constants, and comparing them with the figures obtained by other methods. Hydrochloric acid was used as a standard of comparison. The initial action of acids is, in all cases, to increase the activity of the diastase, an effect which has been noticed by Duggan and others, and is probably due to a slight

alkalinity of the starch. The following values were obtained for the affinity constant K:—

Formic acid .... $K = 0.025$
Acetic acid. .... $K = 0.00146$
Propionic acid .... $K = 0.0006$
Butyric acid............ $K = 0.00071$
Isobutyric acid .... $K = 0.0008$

These values are in the same order as those obtained by Ostwald, with the exception of the two butyric acids, which he found to have nearly the same value.

By comparing the action of the sodium salts of the fatty acids with that of sodium hydroxide, the amount of free hydroxyl, and therefore the percentage of the salt that has suffered hydrolysis, can be determined, as the salt yields free acid and free base, and the latter breaks up completely into Na and OH ions. It was found, in this way, that the percentage hydrolysed was proportional to the affinity of the acid, but no careful or extended tables were prepared.

In the presence of the salt of a weak acid, very large quantities of acid can be added without affecting the diastase, except to a very limited degree. Quantitative measurements show that this behaviour is in keeping with the dissociation theory, for, as the work of Arrhenius indicates, the presence of a salt in a solution of its acid prevents the dissociation of the latter to a degree depending on the amount of salt present. H. C.

Apparatus for Regulating Diminished Pressures. By F. KRAFFT (*Ber.*, **27**, 1823).—The regulator for diminished pressures, described by the author 12 years ago (*Ber.*, **15**, 1693), consists of a large vessel with two taps, not of the large vessel alone, as Kahlbaum states (this vol., ii, 349). J. B. T.

Mechanical Agitator. By C. MAULL (*Ber.*, **27**, 1732—1733).— In this instrument, the bottle to be agitated is placed horizontally and then shaken by means of an eccentric attached to a wheel driven by a small turbine. A. H.

Inorganic Chemistry.

Physical Properties of pure Nitrous Oxide. By P. VILLARD (*Compt. rend.*, **118**, 1096—1099).—Pure nitrous oxide is obtained either by preparing the hydrate, which is afterwards allowed to decompose, or by fractionating the compressed or liquefied gas. In the latter case the gas is passed through suitable absorbing and drying agents, and is then liquefied, the nitrogen that accumulates above the liquid nitrous oxide being allowed to escape from time to time. The liquid is then allowed to boil in order to expel the greater

part of the dissolved gas, is next passed into another tube, which is first washed with portions of the liquid, and is finally freed from the last traces of dissolved gas by prolonged ebullition.

The liquid thus obtained is free from less liquefiable gases, its maximum vapour pressure is independent of the volume of the vapour, and a small increase of pressure causes complete liquefaction. The densities of the gas and of the liquid at various temperatures are as follows:—

Temperature ..	0°	5°	10°	17·5°	26·5°	32·9°	34·9°	36·3°
Density of liquid	0·9105	0·885	0·856	0·804	0·720	0·640	0·605	0·572
„ gas..	0·0870	0·099	0·114	0·146	0·207	0·274	0·305	0·338

The critical temperature of pure nitrous oxide is 38·8°, a value higher than that obtained by previous observers. The critical volume is 0·00436, the critical density 0·454, and the critical pressure 77·5 atmospheres.   C. H. B.

Volatility of Borax. By S. WALDBOTT (*J. Amer. Chem. Soc.*, **16**, 410—418).—From the author's experiments, it is conclusively shown that borax glass is decidedly volatile at a white heat, particularly when heated in open crucibles.

Even basic borates are sensibly volatilised, which fact must not be lost from view in the analysis of borates by Rose's and Schaffgotsch's processes.   L. DE K.

Volatility of Sodium Fluoride. By S. WALDBOTT (*J. Amer. Chem. Soc.*, **16**, 418—420).—The author has proved by a series of experiments that sodium fluoride contained in a platinum crucible cannot be heated in the full flame of a bunsen burner without sensibly losing in weight.   L. LE K.

Compounds of Ammonia and Silver Salts. By JOANNIS and CROIZIER (*Compt. rend.*, **118**, 1149—1151).—When ammonia gas is passed over a metallic salt it is difficult to procure complete saturation, but if when no further development of heat takes place the tube is cooled so that the ammonia liquefies and comes into contact with the salt, complete combination takes place. The tension of dissociation of the products is given by the formula $\log P = a/T + b \log T + c$, in which P is the pressure in centimetres of mercury; T the absolute temperature, and a, b, and c are constants which have to be determined for each compound. The values of these constants are given for the compounds described.

Silver bromide yields three white solid compounds, $AgBr,3NH_3$; $2AgBr,3NH_3$; and $AgBr,NH_3$. They dissociate under the ordinary pressure at 3·5°, 34°, and 51·5° respectively.

Silver iodide yields a white solid compound, AgI,NH_3, in addition to the already known $2AgI,NH_3$. Under the ordinary pressure they dissociated at 3·5° and 90° respectively.

Silver cyanide forms the compound $AgCN,NH_3$, which is very soluble in liquid ammonia at −10°. Under the ordinary pressure, its

temperature of dissociation is 102°; at 100° its dissociation pressure is 690 mm. and not 550 mm. as stated by Isambert.

Silver nitrate forms three compounds, $AgNO_3,3NH_3$; $AgNO_3,2NH_3$; and $AgNO_3,NH_3$. The first is very soluble in liquid ammonia below $-10°$, and dissociates at 63° under normal pressure. The second compound dissociates under normal pressure at about 170°, but the phenomena are irregular. C. H. B.

Changes during the Remelting of Lead-tin Alloys. By B. WIESENGRUND (*Ann. Phys. Chem.*, [2], **52**, 777—792).—Rudberg (1830) observed that when alloys of lead and tin are cooled, an inserted thermometer remains stationary at two different points, the upper point varying with the composition of the alloy, the lower point being the same for all alloys, and being about 187°. The alloy of the composition $PbSn_3$ only gives the latter point, this being the melting point of the alloy in question. These results were confirmed by Wiedemann (1878). The author has submitted these alloys to a further examination, and his results are given in the following table. In this table, the first column, I, gives the composition of the alloy under examination, II the specific gravity directly determined, III the specific gravity calculated on the assumption that no change in volume takes place on mixing the two metals, column IV contains the differences of the second and third, V the lower, and VI the higher stationary points shown by the thermometer immersed in the cooling alloy.

I.	II.	III.	IV.	V.	VI.
$PbSn_{12}$..............	7·6660	7·8150	1490	185·2°	206·7°
$PbSn_5$	7·9995	8·3497	3502	184·5	191·0
$PbSn_4$	8·0815	8·5302	4487	184·0	186·6
$PbSn_3$	8·3636	8·8524	4888	183·0	183·0
$PbSn_2$	8·7298	9·1903	4605	182·2	202·0
$PbSn$	9·4320	9·8770	4450	181·3	242·0
Pb_2Sn	10·0380	10·4487	4107	180·0	273·0
Pb_3Sn	10·3033	10·7001	3968	178·3	284·0
$Pb_4Sn + 5$ grams Sn..	10·4122	10·7770	3648	176·0	289·0
Pb_4Sn	10·5371	10·8414	3043	174·3	295 0
Pb_5Sn	10·6620	10·9322	2702	172·4	305·0
$Pb_{12}Sn$..............	11·1825	11·2493	0668	—	317·0

It will be seen that the maximum difference between the observed and calculated specific gravities is obtained with the alloy $PbSn_3$, for which the lower and higher melting points coincide. If any one of the above alloys, with the exception of $PbSn_3$, is remelted several times over, and the melting points again determined a slight rise is in each case found to have taken place, but in no case is a rise of more than one degree observed. H. C.

Stability of Dilute Solutions of Mercuric Chloride. By L. VIGNON (*Compt. rend.*, **118**, 1099—1101; compare this vol., ii, 93).—

When mercuric chloride is heated at 80° for 60 hours, the residue has the composition represented by the formula $HgCl_2$. Repeated evaporation of a 0·1 per cent. aqueous solution in a vacuum has no effect on the solubility of the salt. A solution of this strength undergoes no change after contact with purified air for 60 days. When such a solution is partially or fully exposed to ordinary air the rate of alteration is smaller the more completely the air is excluded. (Compare Tanret, this vol. ii, 93).

When sodium hydroxide, sodium carbonate, or ammonia, are added to dilute solutions of mercuric chloride in quantity insufficient for complete precipitation, the results are irregular so far as concerns the rate of precipitation and the character of the precipitate. Sometimes precipitation is immediate, and at other times it requires several hours; sometimes the precipitate is dense and compact, and at others it is finely divided and remains in suspension. The quantity of mercury precipitated is always higher than the calculated quantity, and it increases with the time, a result which is due to the formation of oxychlorides and chloramides containing a high proportion of mercury.   C. H. B.

Production of Metallic Films specially adapted for covering Aluminium. By C. GOTTIG (*Ber.*, **27**, 1824—1826).—Aluminium becomes covered with a hard film of copper on rubbing it with tin dipped in copper sulphate solution, the deposit increases in thickness if the coated metal is suspended in a dilute copper salt solution. Aluminium is covered with tin by rubbing it with brass moistened with solutions of certain tin salts, such as ammonium stannichloride, $SnCl_4,2NH_4Cl$; in this case, too, the deposit increases in thickness when the metal is suspended in a tin salt solution of suitable concentration. Aluminium which has been coated with copper as above described, when suspended in a solution of a tin salt, receives a coating of tin over the copper.   J. B. T.

Iron Phosphide. By L. M. DENNIS and B. S. CUSHMAN (*J. Amer. Chem. Soc.*, **16**, 477—485).—See this vol., ii, 400.

Molecular Transformations of some Chromium Compounds. By A. RECOURA (*Compt. rend.*, **118**, 1146—1149).—The author confirms the statement of Favre and Valson, that when the green solutions of the basic sulphate $[Cr_4O(SO_4)_4]OH$ are mixed with barium chloride in the cold, there is an immediate precipitation of one-third of the sulphuric acid only. It follows that the green solution has the composition $[Cr_4O(SO_4)_4]SO_4 + H_2SO_4$, the basic salt being the sulphate of the complex radicle $[Cr_4O(SO_4)_4](OH)_2$. This base can be obtained by treating the green solution with the proper quantity of alkali; it is soluble, and its solution has a more brilliant green colour than the original solution.

$[Cr_4O(SO_4)_4](OH)_2$ diss. $+ H_2SO_4$ diss. $=$
   $[Cr_4O(SO_4)_4]SO_4$ diss. $+ H_2O$ . . . .   develops $+14\cdot2$ Cal.
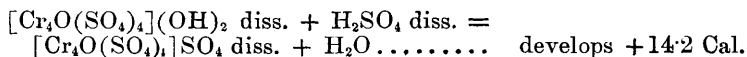
When the solution of this base is mixed with a quantity of alkali

equivalent to the sulphuric acid present in the radicle, it is decomposed, and the hydrate $Cr_2O(OH)_4$ is precipitated. When this hydrate is dissolved in sulphuric acid, the latter gives normal reactions, and hence the salt $Cr_2O(SO_4)_2$ is an ordinary basic sulphate. The green sulphate of the heated solutions, however, is not a sulphate of a hydrate $Cr_4O(OH)_{10}$, but is the normal sulphate of *sulphochromylhydroxide* $[Cr_4O(SO_4)_4](OH)_2$.

By means of the action of sodium hydroxide, the author finds that

$Cr_2(OH)_6 + aq. = Cr_2O(OH)_4 + aq., +$
H_2O liq. . . . . develops -1.25 Cal.
$Cr_2(OH)_6 + aq. = Cr_2O(OH)_4 + aq., +$
H_2O sol. . . . . ,, $+0.18$,,
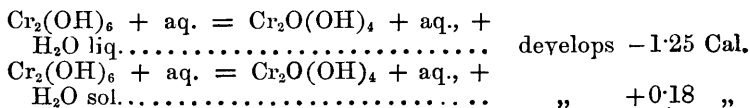
It is probable that the actual development of heat is much greater, but is masked by the heat absorbed by the preliminary separation of several molecules of water of hydration. The heat of neutralisation of the precipitated normal hydrate decreases, and tends towards the value corresponding with $Cr_2O(OH)_4$, and the dehydration may even go beyond this point, for, after a long time, an alkaline solution of chromium hydroxide gradually deposits the oxide insoluble in dilute acids. Moreover, when precipitated chromium hydroxide is dissolved in excess of sodium hydroxide, the heat of neutralisation is lower the longer the time that has elapsed since the preparation of the solution, the value for $2H_2SO_4$ dil. $+ Cr_2O_3$ aq. being $+ 25$ Cal. after 10 minutes, $+ 22.5$ Cal. after 25 minutes, and $+ 15.8$ Cal. after 70 minutes. C. H. B.

Chlorochromates and Amidochromates. By S. LÖWENTHAL (*Zeit. anorg. Chem.*, **6**, 355—368).—Ammonium chlorochromate is prepared by Peligot's method by the action of chromyl chloride on an aqueous solution of ammonium chloride. It crystallises well, melts easily, is red, and dissolves in water with a crackling noise.

Lithium chlorochromate, $LiClCrO_3$, is obtained by the action of chromyl chloride on lithium chromate in aqueous solution. It crystallises in yellowish-red, lustrous crystals belonging to the monosymmetric system $a : b : c = 1.1589 : 1 : ?, \beta = 64° 50'$. It melts to a reddish-brown mass.

Magnesium chlorochromate is obtained by adding chromyl chloride to a concentrated solution of magnesium chloride and allowing the mixture to remain some time in a freezing mixture. It separates in reddish-yellow crystals with $9H_2O$. It is also obtained by adding solid chromic acid and a little acetic acid to a concentrated solution of magnesium chloride, and then cooling the mixture. When prepared by this method, it separates in red to reddish-brown crystals with $5H_2O$, does not give up its water of crystallisation when allowed to remain over sulphuric acid, and is very hygroscopic.

Zinc chlorochromate forms small, yellowish-red crystals with $9H_2O$, decomposes on recrystallisation, is very hygroscopic, and dissolves easily in water and acids. It decomposes with evolution of chlorine if left over sulphuric acid, and also when gently heated in a tube, or at the ordinary temperature in a vacuum desiccator.

The author failed to prepare the corresponding salts of barium and strontium by the method described above for magnesium chlorochromate.

Potassium amidochromate is prepared by the method described by Heintze, by passing dry ammonia into the chlorochromate. It crystallises in tablets belonging to the monosymmetric system; $a : b : c = 1\cdot02832 : 1 : 1\cdot7751$, $\beta = 88° 3'$.

Ammonium amidochromate crystallises in yellowish-red tablets belonging to the monosymmetric system, $a : b : c = 1\cdot0310 : 1 : 1\cdot8243$, $\beta = 85° 43'$. It dissolves easily in water with a crackling noise.

·*Lithium amidochromate* crystallises in purplish-red asymmetric prisms, $a : b : c = 0\cdot5578 : 1 : 0\cdot5548$, $\alpha = 81° 56'$, $\beta = 91° 0\frac{1}{2}'$, $\gamma = 83° 29\frac{1}{2}'$. It is easily soluble, and melts when gently heated.

Magnesium chlorochromate, after remaining six months over calcium chloride and sulphuric acid, still contains water, and is converted into a brown mass without any evolution of chlorine or chromyl chloride taking place. On treating this dried compound with ammonia, a yellow product is obtained which contains ammonia and chlorine, and is possibly a double compound of magnesium amidochromate and magnesium chlorochromate. The author was unable to prepare zinc amidochromate.

When potassium amidochromate is mixed with concentrated solutions of acetate of magnesium, zinc, or manganese, and allowed to evaporate in a desiccator, it crystallises out unaltered. With the acetates of lead, barium, strontium, and calcium, the corresponding chromate is at once formed. With mercuric acetate, a reddish-yellow precipitate is obtained which has the composition $Hg_3(CrO_3)_2NH_2$. Potassium amidochromate forms double salts with magnesium sulphate, which are bright yellow, easily soluble, and crystallise extremely well.   E. C. R.

Action of Phosphorus Pentachloride on Molybdic acid. By E. F. Smith and G. W. Sargent (*Zeit. anorg. Chem.*, **6**, 384—385).— When molybdic acid ($1\cdot5$ grams) is heated with phosphorus pentachloride (10 grams) in an atmosphere of chlorine at 175°, and the product gently warmed in a current of chlorine, phosphorus oxychloride, and a compound of the composition $MoCl_5,PCl_5$, are obtained. The latter sublimes in greenish-black crystals, and is very easily decomposed. Piutti (*Gazzetta chim.*, **9**, 538), under slightly different conditions, obtained a similar compound to which he assigned the composition $MoCl_5,POCl_3$.   E. C. R.

Complex Inorganic acids. VI. Decomposition-products of Phospholuteotungstic acids. By F. Kehrmann and E. Böhm (*Zeit. anorg. Chem.*, **6**, 386—391).—The authors have already shown that the yellow alkali salts of phospholuteotungstic acid, $3RO,P_2O_5,18WO_3$, are converted by the action of alkalis into colourless salts of the formula $5RO,P_2O_5,17WO_3$. They have now examined this reaction quantitatively, and find that it takes place according to the equation

$$3K_2O,P_2O_5,18WO_3 + 3K_2O = 5K_2O,P_2O_5,17WO_3 + K_2WO_4.$$
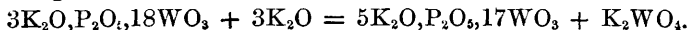
The luteo-salt, dissolved in a small quantity of cold water, is mixed with a cold saturated solution of potassium hydrogen carbonate until it is decolorised. After remaining a quarter of an hour, the precipitated salt is collected and dried, and the phosphoric and tungstic acids determined in the filtrate. The small quantity of phosphoric acid found in the filtrate, and the excess of tungstic acid over that required by the above equation are in the ratio 1 : 18·7, showing that the phosphoric acid is present in the form of the salt $K_2O,P_2O_5,17WO_3$.

The salt $(NH_4)_2O,P_2O_5,17WO_3$, when heated with excess of cold 10 per cent. hydrochloric acid and then gradually warmed to boiling as long as a white precipitate is formed, gives the following products. The white precipitate, about 4 per cent., is ammonium phosphoduo-decitungstate, $3(NH_4)_2O,P_2O_5,24WO_3 + $ aq. From the filtrate, 95 per cent. of the ammonium salt of the luteo-acid is obtained by precipitation with ammonium chloride, and finally with quinoline hydrochloride. The filtrate from this second precipitation contains about 0·25 per cent. of phosphoric acid.

Analyses of the ammonium and potassium salts of the 17-series show, without doubt, that they have the composition

$$5(NH_4)_2O,P_2O_5,17WO_3 + 16H_2O$$
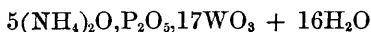
and $5K_2O,P_2O_5,17WO_3 + 21$ or $22H_2O$.   E. C. R.

Chlorides of Zirconium. By F. P. VENABLE (*J. Amer. Chem. Soc.*, **16**, 469—475).—As it is very doubtful whether zirconium tetrachloride has hitherto been obtained pure, that is, free from oxychloride, the author has reinvestigated the matter. He finds that when the crystals, obtained by dissolving the oxide in strong hydrochloric acid and recrystallising from the same solvent (Abstr., 1892, 412), are dried at 100—110° in a current of dry hydrogen chloride free from air, the substance first melts, and, after the loss of the moisture and excess of hydrogen chloride, resolidifies to a hard white mass which is very hygroscopic. If the drying is done very slowly, fine crystals are obtained. These crystals, giving 52·7 per cent. of ZrO_2 on ignition in the air, are pure zirconium tetrachloride. This substance is very unstable, forming basic or oxy-compounds on exposure to air or moisture.

If dilute hydrochloric acid is used for dissolving the oxide, zirconium oxychloride, $ZrOCl_2$ is formed as a white powder insoluble in hydrochloric acid but soluble in water.   L. T. T.

Double Bromides of Palladium. By E. F. SMITH and D. L. WALLACE (*Zeit. anorg. Chem.*, **6**, 380—383).—The double bromides are obtained by dissolving dry palladium bromide and equivalent quantities of the metallic bromide in water containing hydrogen bromide, and evaporating the mixture.

Potassium palladium bromide, K_2PdBr_4, crystallises in lustrous, reddish-brown needles, is anhydrous, very stable, and remains unchanged on exposure to air. When treated with bromine at 70°, with the object of obtaining the salt K_2PdBr_6, it remains unaltered, but crystallises from the solution with $1H_2O$. These crystals are long,

dark-brown needles, which quickly lose their lustre on exposure to air, and are converted into a reddish-brown powder.

Ammonium palladium bromide crystallises in beautiful olive-brown orthorhombic forms. It is anhydrous, and quite stable on exposure to air.

Sodium palladium bromide crystallises with difficulty in large, dark-red tablets containing 14·6 per cent. H_2O, and very easily deliquesces.

Strontium palladium bromide, $SrPdBr_4 + 6H_2O$, crystallises in short, black prisms, and is stable on exposure to air.

Manganese palladium bromide, $MnPdBr_4 + 7H_2O$, crystallises in black crystals similar in form to the ammonium salt. It is extremely soluble.

The authors were unable to obtain crystalline double haloïd-salts of zinc and cadmium with palladium. E. C. R.

Ruthenium and its Nitroso-chlorides. By J. L. HOWE (*J. Amer. Chem. Soc.*, **16**, 388—396).—Ruthenium nitroso-chloride is readily prepared by boiling the oxide RuO_4 with aqua regia in a reflux apparatus, and evaporating the solution. It forms stable double salts with the alkaline chlorides; 100 parts water at 25° dissolve 12 parts of the potassium double salt (Joly, Abstr., 1889, 352), and 80 parts at 60°. Of the ammonium salt (Joly, Abstr., 1891, 401), 100 parts of water dissolve 5 parts at 25°, 22 parts at 60°. *Rubidium ruthenium nitroso-chloride*, $2RbCl,RuCl_3\cdot NO$, forms a pale purple powder, which may be recrystallised from boiling water in almost black crystals resembling those of the potassium and ammonium salts. When a solution is evaporated over sulphuric acid, the *hydrated salt* crystallises with $2H_2O$ in dark purple crystals. It loses its water on heating or over sulphuric acid. 100 parts of water dissolve 0·57 part at 25°, and 2·13 parts at 60°. *Cæsium ruthenium nitroso-chloride* forms a pale purple powder or minute crystals. 100 parts of water dissolve 0·20 part at 25°, and 0·56 part at 100°. The *hydrated salt*, $2CsCl,RuCl_3\cdot NO + 2H_2O$, yields large, dark purple crystals very soluble in water, 100 parts of water dissolving 105·8 parts of salt.

When the potassium salt is heated, decomposition does not commence until above 250°, and then the chlorine and nitroso-group are both separated together. Solutions of the nitroso-chlorides are not acted on by carbamide, or reduced by ferrous sulphate, or by cuprous or stannous chlorides. Hydrogen peroxide is without action in acid solutions, but when it is added to alkaline solutions oxygen is evolved, and the solution decolorised. Permanganates are reduced by boiling with alkaline solutions, nitric acid being amongst the products. Sodium hypobromite causes evolution of gas, and on acidifying with hydrochloric acid ruthenium tetroxide and bromine are evolved. Potassium cyanide appears to form a double salt. Mercurous and silver salts give buff precipitates, but the other heavy metals are not precipitated.

The nitroso-chlorides may be distinguished from the trichlorides as follows. The solutions are rose-coloured, and become salmon-pink on dilution; excess of alkali does not cause a precipitate; no purple colour is given on boiling with a thiocyanate; there is no reaction with

ammonia and sodium thiosulphate; boiling a neutral solution with potassium ferrocyanide yields a very characteristic deep brown coloration.

No higher chloride than the trichloride could be obtained. The nitroso-chloride is produced by the method described by Claus for preparing his red salt, which he thought to be the tetrachloride.

The rubidium and cæsium hydrated double salts were crystallographically examined by N. D. Clark. They are isomorphous, and crystallise in the monoclinic system. The axial ratios obtained were.

$2CsCl,RuCl_3 \cdot NO,2H_2O$, $a : b : c = 1 \cdot 698 : 1 : 1 \cdot 177$ and $\beta = 76° 11'$.
$2RbCl,RuCl_3 \cdot NO,2H_2O$, $a : b : c = 1 \cdot 692 : 1 : 1 \cdot 242$ and $\beta = 76° 50 \cdot 5'$.

L. T. T.

Mineralogical Chemistry.

Composition and Origin of Natural Gas. By F. C. PHILLIPS. (*Amer. Chem. J.*, **16**, 406—429).—Continuing his researches on the phenomena of oxidation and chemical properties of gases (this vol, ii, 293, 294, and 367), the author has analysed (for method see this vol., ii, 401) a large number of natural gases from various parts of America, and one from Vancouver. These all contained from 90—99 per cent. of paraffins, and from a trace to 3·6 per cent. of carbonic anhydride, the remainder being nitrogen. A trace of hydrogen sulphide was detected in one sample, and a trace of oxygen in several, but in no case was any hydrogen or ammonia found. The absence of hydrogen was proved by passing the gas through dry palladium chloride (which is at once reduced by hydrogen), and also through solutions of palladium chloride, platinum chloride, and ammoniacal silver nitrate, when no precipitates were formed. These tests and passing through bromine water showed the absence of carbon monoxide, olefines, or members of the acetylene series. These natural gases were also not ignited by platinised asbestos below about 300°. Experiments specially made showed that natural gas was ignited by platinised asbestos at 40—50° when it contained 5 per cent. hydrogen, at 80—90° when 2·5 per cent., at 210—220° when 0·5 per cent., and only at 270—290° when it was free from hydrogen. The paraffins present were chiefly methane, the percentage composition, as determined by combustion, varying between C = 74·96 H = 25·04 and C = 78·14H = 21·86, though C = 77 per cent. was exceeded in only two out of 17 gases.

With the aim of throwing some light on the probable origin of natural gas, 50 grams of an air-dried fucus were steeped in water and then introduced into a flask, the latter filled with water free from air and connected with a bell jar over a mercury trough. No gas appeared till the third day, when rapid evolution of gas commenced, and continued in gradually decreasing rate till the end of 10 days,

when 803 c.c. of gas had been collected, and the evolution had apparently ceased. The analysis of the gas evolved gave

	First 300 c.c.	Second 300 c.c.	Remaining 203 c.c.
Carbonic anhydride..	18·23	32·47	53·44
Methane...........	0·30	0·28	0·08
Hydrogen..........	62·24	49·97	42·02
Nitrogen...........	19·23	18·28	4·46

The apparatus was, however, still kept set up for a further two and a half years, when another 30 c.c. of gas had collected in the receiver, and this was found to consist of almost pure methane. The author considers that this extremely slow secondary decomposition of vegetable matter at about ordinary temperatures and in the absence of air must not be ignored when considering the probable sources of natural gas. L. T. T.

Artificial Preparation of Hæmatite. By H. ARCTOWSKI (*Zeit. anorg. Chem.*, **6**, 377—379).—A current of ammonium chloride vapour when passed over oxide of iron, heated to dull redness, converts the oxide into crystalline hæmatite. Ferric oxide heated at 350° absorbs ammonium chloride vapour, and melts to a black mass, from which ferric chloride soon distils. The residue absorbs water from the air, and is a mixture of ammonium chloride and ferric chloride. At 600°, the ferric oxide is partially converted into small crystals, and then mechanically absorbs ammonium chloride without melting. At 700° the ferric oxide becomes crystalline. The crystals are of the same form as the hæmatite crystals from Elba. The author points out that the gases of fumaroles contain ammonium chloride, and the fissures in the vicinity are generally covered with crystals of hæmatite. E. C. R.

Physiological Chemistry.

Effects of Diminution of Oxygen on the Organism. By T. ARAKI (*Zeit. physiol. Chem.*, **19**, 422—475), and by F. HOPPE-SEYLER (*ibid.*, 476—481); compare Abstr., 1893, ii, 136, 428.—In previous communications it has been shown that diminution in the supply of oxygen to an animal will cause the occurrence in the urine of albumin, sugar, and lactic acid. Poisoning by carbonic oxide or other toxic agents produces the same result in the same way. In the present communication these observations are continued.

Certain observers have stated that sugar and lactic acid occur in the urine after severe hæmorrhages. The experiments here recorded on rabbits and dogs, in which large quantities of blood were removed, did not support this view. The urine, however, was usually albuminous.

The next series of experiments relate to the effect of diminution of oxygen supply on the alkalinity of the blood and the hepatic glycogen. The lessened supply of oxygen was produced in some cases by poisoning with carbonic oxide, in others by diminishing the amount of oxygen in the inspired air. In all cases, rabbits were used, and the result found was that the hepatic glycogen was markedly diminished, thus supporting the views of those who hold that lactic acid originates from glycogen. The alkalinity of the blood was lessened. A similar result follows the administration of amylic nitrite. The percentage of glycogen in the muscles also sinks. The quantity of urea excreted greatly diminishes during carbonic oxide poisoning. A few experiments support the statement first made by Hoffmann (*Arch. exp. Path. Pharm.*, **7**, 233), that the kidneys of an animal poisoned by quinine or carbonic oxide are unable to form hippuric acid from glycocine and benzoic acid.

In another series of animals (dogs and rabbits), sodium lactate was administered. If the animals were normal, little or no lactic acid was found in the urine, which was strongly alkaline from carbonate formed from the lactate. If the animals were poisoned with carbonic oxide, the urine was strongly acid, and contained lactic acid.

Minkowski has shown that in animals from which the liver has been removed, lactic acid is formed in the urine; this can only be explained by supposing that interference with the blood circulation produces a diminished supply of oxygen.

Hoppe-Seyler's remarks are of a commendatory nature; they also include the description of an apparatus (with figure) by means of which air containing but little oxygen can be given to an animal.

W. D. H.

Diffusion of Gases in Water. By F. HOPPE-SEYLER (*Zeit. physiol. Chem.*, **19**, 411—421; compare Duncan and Hoppe-Seyler, Abstr., 1893, ii, 62, 81).—A few experiments are recorded which show the extreme slowness of diffusion of the atmospheric gases in water. This subject derives physiological importance from the consideration of the possibilities of life in marine animals at great depths.

W. D. H.

Digestibility of Fresh Brewer's Grains and Meat Meal, Earth Nut Cake, Extracted Caraway and Fennel Seeds, Rye Bran and Dried Grains, Rice Meal, Cotton Seed Meal, Extracted Aniseed, Cocoa Nut Meal, and Poppy Cake. By G. KÜHN and others (*Landw. Versuchs-Stat.*, **44**, 1—187).—The results were obtained by direct experiments with bullocks during the years 1873—1892. The amount and composition of food and fæces, the live weight of the animals, &c., are given in tables.

N. H. M.

Digestion of Nitrogenous Food Constituents by Treatment with Gastric Juice and Pancreas Extracts. By G. KÜHN and others (*Landw. Versuchs-Stat.*, **44**, 188—256).—Stutzer's method for determining digestibility consisted in subjecting the substance to the action of 250 c.c. of a pepsin solution (*Journ. f. Landw.*, 1880, **28**, 195 and 435) for 24 hours. Experiments were instituted by the

authors to ascertain the effect, if any, of varying the amount of pepsin, the duration of the action and the amount of acid. For some foods it was found that for every two grams, 500 c.c. of pepsin solution, to which hydrochloric acid is gradually added to the extent of 1 per cent. (as recommended by Stutzer) should be employed, and that the action should be continued for at least 48 hours. With most foods, as the residues of fennel, anise, caraway seeds, &c., the action must be prolonged to 72, or even 84 hours. Foods not hitherto examined should be first tested in order to ascertain whether 48 hours is sufficient.

Pfeiffer (*Journ. f. Landw.*, **31**, 1883, 221), in experimenting with sheep, found that they digested more nitrogenous matter than Stutzer's method indicated, and proposed the employment of pancreas solution after pepsin (*Zeit. physiol. Chem.*, 1885, **9**, 211). He found that 20—30 per cent. more nitrogenous matter was digested, and that the results then approximated more closely to those obtained with live animals. Stutzer concluded that the two solvents dissolved different nitrogenous substances.

Inasmuch as it is now shown that the 24-hour treatment with pepsin solution was insufficient, and as Stutzer himself showed that a pancreas extract alone had not a greater solvent power than pepsin. it seemed possible that the action of pancreas solution on a substance already treated with pepsin might be due to the alkali employed. This is now shown to be the case by comparative experiments. With hay, linseed cake, and cotton cake, there was generally less undissolved nitrogenous matter after treatment with soda than with pancreas, and in every case both the pancreas and the soda dissolved nitrogenous matter left undissolved by pepsin. In the case of ethereal oil residues, the pancreas dissolved considerably more than the soda; this is due to the resinous matters they contain, which are first attacked by soda and then digested by the pancreas.

When the new method (more prolonged treatment with pepsin) was compared with Stutzer's method (successive treatment with pepsin and pancreas) it was found that in twelve experiments eight gave higher results (undissolved substances) with Stutzer's method, and four with Kühn's method.

It is concluded that pepsin solutions will dissolve all the really digestible nitrogenous matter of foods, unless, as in the case of umbelliferous seeds, there is some hindrance. Treatment with pancreas is unnecessary, and the use of soda which it involves is unsafe.

The results of 22 feeding experiments with bullocks show the correctness of this view, and that the nitrogenous matter of food which is not attacked by pepsin is completely separated in the intestines. In artificial digestion, any further amount dissolved by pancreas, after treatment with pepsin, is due to the action of the soda.

The analytical results are given in tables, showing the amount of pepsin solution employed and the duration of the experiments, &c.

The experiments were made in 1882—92. N. H. M.

Feeding and Respiration. Experiments with Bullocks on Fat Formations from Carbohydrates, and the Relations of Food to the Elimination of Hydrocarbons. By G. KÜHN and others (*Landw. Versuchs-Stat.*, **44**, 257—582).—The object of the experiments was not so much to confirm or refute the formation of fat from carbohydrates as to obtain general knowledge as to the relation between fat formation and food. As regards the production of fat from proteïds, the results of v. Voit, and v. Pettenkofer, and many others, were supposed to have established it, until Pflüger recently (*Arch. Ges. Physiol.*, **51**, 1891, 229) pointed out that v. Voit attributed too low a value for the nitrogen of flesh and too high a value for the carbon. The question of fat formation from proteïds must still be considered an open one. The question of the formation of hydrocarbons is also considered, Tappeiner and others having maintained that cellulose is not digested, or only partly digested by herbivora, but that it is probably entirely transformed by micro-organisms into gaseous products of no use to the animal. The apparatus employed in the experiments is described in detail and with sketches; it consists of a respiration case, an arrangement for measuring the air passing through the case, instruments for estimating the carbon in the air, and a ventilator by means of which a constant current of air was passed through the case.

There were four series of experiments with bullocks. In series 1, the food given was hay and wheat starch; in 2, clover hay, oat straw, wheat starch, and wheat; in 3, hay and starch meal; and in 4, hay, meat-meal free from fat, and starch meal.

In considering the results, it is pointed out that a ration which maintains an animal at a constant weight does not necessarily keep it in equilibrium internally, since there is always a renewal of hair, skin, and hoof going on. Henneberg estimated a daily loss of nitrogen (4·5 grams) and carbon (12·5 grams) from hair falling off in summer.

The results confirm the view that the amount of albumin given in food controls the decomposition, but not the deposition of albumin, and that any increase of food over the smallest quantity required gives rise to a production of fat; it is immaterial whether the excess of food is nitrogenous or non-nitrogenous. Bullocks fed with 31·04 kilos. of digestible organic matter with a nutritive ratio of 1 : 4·5—7·2 deposited 2·049 kilos. of fat, whilst bullocks with 30·52 kilos. of digestible food with a nutritive ratio of 1 : 14·0—17·4 deposited ?·138 kilos. of fat. A given amount of gluten may thus be replaced by a similar amount of starch without affecting the amount of fat formed. Within certain limits, fat production progresses approximately with the excess of food given. This is shown by the following average results:—

		Organic matter digested.	Fat deposited.
Means of Expt.	1— 5	9·10 kilos.	0·446 kilo.
,,	6—10	9·73 ,,	0·640 ,,
,,	11—14	10·78 ,,	0·852 ,,

For every kilogram of starch meal in excess of food actually

required there will be a deposition of about 0·2 kilo. of fat : how much of this fat is formed directly from starch and how much (through the saving effect of starch) from the fat of the food, and from decomposed albumin remains undecided. The experiments show conclusively that fat is formed from starch meal.

As regards the production of hydrocarbons, there was always a certain amount of gaseous hydrocarbon, but not in anything like the quantity to be expected according to Tappeiner's results. Nitrogenous food does not seem to produce hydrocarbons to any extent, if at all, but starch and other non-nitrogenous foods seem to give rise to their formation to about the same extent as cellulose ; so that cellulose is practically as nutritive as starch, and the so-called non-nitrogenous extracts, and there is no reason at all why its nutritive value should be called in question. The conditions of the experiments made it impossible to ascertain whether fat when undergoing change in the intestines yields any hydrocarbon.   N. H. M.

Putrefaction of Proteïd in the Intestine. By K. Schmitz (*Zeit. physiol. Chem.*, **19**, 378—400 ; 401—410).—The first paper relates to the influence of milk, kephir, and cheese on intestinal putrefaction. That milk exerts an anti-putrefactive influence is well known, although observers differ as to the constituent to which milk owes this property. The criterion of the amount of putrefaction taken is the quantity of ethereal hydrogen sulphates in the urine. Judged by this standard, cheese lessens putrefaction. This effect, however, is not produced by caseïn, and the lactose is held to be the responsible agent in cheese as well as in milk and kephir.

The second paper relates to the influence of hydrochloric acid on putrefactive processes. Administration of the acid in dogs produced no result ; but in men it lessened the output of ethereal hydrogen sulphates. This difference of action in the two animals is considered to be due to the fact that the acid in the gastric juice of the dog is already present in sufficient quantity to produce a maximum effect.   W. D. H.

Fats of Human Milk. By E. Laves (*Zeit. physiol. Chem.*, **19**, 369—377 ; compare Ruppel, this vol., ii, 326).—The fat of human milk is very poor in volatile acids and acids soluble in water, but rich in unsaturated acids. The fat contained

> 1·4 per cent. of volatile acids.
> 1·9   ,,   acids soluble in water.
> 49·4   ,,   unsaturated acids.

The volatile acids contain about equal quantities of caproic, caprylic, and capric acid, and the merest traces of butyric acid. The acids mainly present are palmitic, stearic, and oleic acids (as is usual in animal fats), and one or more acids of lower molecular weight, probably myristic acid. The melting point of these fatty acids lies between 37° and 39°, of the fat itself 30—31°. There are therefore important differences in the fats of cow's milk and of human milk.   W. D. H.

Carbohydrates of Normal Urine. By K. BAISCH (*Zeit. physiol. Chem.*, **19**, 339—368; compare Abstr., 1893, ii, 542) —The two carbohydrates in normal urine, identified by a very complete examination of their reactions and properties, are glucose and a dextrin-like substance (animal gum). The quantity of glucose averages 0·005 per cent., and of total carbohydrate reckoned as glucose about twice that amount.

There appears also to be a small quantity of a third reducing carbohydrate, which was not, however, satisfactorily identified.

W. H. D.

Sarcolactic acid in Pathological Urines. By E. SCHÜTZ (*Zeit. physiol. Chem.*, **19**, 482—487).—The detection of small quantities of sarcolactic acid added to the urine is quite feasible. The method employed is described.

Morbid urines from 30 patients suffering from a variety of diseases, some of which previous observers have stated lead to the excretion of sarcolactic acid, were examined always with negative results.

A crystalline compound of zinc was, however, obtained, which might be mistaken for zinc sarcolactate; but analysis showed it could not be such; moreover, it contained nitrogen. The chief substance present in the crystals is considered to be zinc hydroxyphenylacetate, or a mixture of this with zinc hydroxyphenylpropionate; perhaps hippuric acid is present also. W. D. H.

Action of definitely-related Chemical Compounds on Animals. By W. GIBBS and E. T. REICHERT (*Amer. Chem. J.*, **16**, 443—449; compare Abstr., 1890, 280, 813, 1018; and 1891, 1280 and 1393).—Being obliged to abandon this investigation, the authors propose, in this and succeeding papers, to recapitulate and summarise the results they have obtained.

Starting from phenol, the authors find that the substitution of hydroxyl for hydrogen atoms does not materially change, but intensifies, the physiological action, although position-isomerism exerts also a marked influence on intensity and sometimes even on the character of the action. With the phenols, those having the greatest reducing action have generally the greatest physiological action. The substitution of alkyl-radicles for hydrogen changes the mode of physiological action. The substitution of the nitro-group for hydrogen tends both to change and intensify physiological action. With mononitrophenols, the action is mainly on the circulation, and hardly at all on the nervous system, and increases from the ortho- to the para-compound. Further substitution of nitro-groups increases the intensity of action. The nitrobenzenes are somewhat similar in action to the nitrophenols, but less powerful. The nitranilines all stimulate the peripheral ends of the vagi and alter the hæmoglobin of the blood, but have little action on the nervous system, so that, in this case, the action of aniline (mainly nervous) is completely changed by the introduction of the nitro-group. In the toluidines, the result of the introduction of methyl in the aniline is somewhat similar to that of the nitro-group, reducing very much the action on the nervous system, and much increasing that on the vascular system. L. T. T.

Physiological Action of Hydrazine and Dibenzoyldiamide. By P. BORISSOW (*Zeit. physiol. Chem.*, **19**, 499—510).—Curtius showed that hydrazine unites firmly with aldehyde groups. Hence it is important to investigate its action on the organism. Loew (Abstr., 1891, 239) has shown that it rapidly kills seedlings, fungi, and infusoria. In the present experiments, it was subcutaneously injected in dogs. In small doses (0·05 gram of the hydrazine-sulphate per kilo. of body weight) it produced slight stimulation; in large doses (0·1 gram per kilo.) the stage of stimulation was more intense, and followed by depression, ending in coma and death in two days. Given by the mouth, it produced salivation and sickness. The heart went more quickly at first, then slowed gradually and became irregular. The respiratory movements reminded one of asthma. The temperature of the body sinks.

The urine was strongly acid, and contained small quantities of the unchanged hydrazine, a small amount of albumin, in one case bile pigment, and in most cases considerable quantities of allantoin. The saliva, which is abundant, also contained allantoin.

At the autopsy, the most marked sign found was hyperæmia of the intestine, liver and kidneys.

Three experiments were made with bibenzoylhydrazine; its toxic effect is about five times weaker than that of hydrazine. The symptoms differ somewhat from those produced by hydrazine. In one experiment, allantoin was found in the urine. The cause of the excretion of allantoin is considered to be disordered metabolism produced in the liver, so that uric acid is not formed there normally.

W. D. H.

Physiological action of the Compounds of the Cocaïne Series. By P. EHRLICH and A. EINHORN (*Ber.*, **27**, 1870—1873).— Cocaïne, in addition to its action as an anæsthetic, produces a very marked change in the liver, which is characterised by a great increase in the volume of that organ and a specific degeneration of the liver cells (Ehrlich, *Deut. med. Woch.*, 1890, No. 32). This property is not possessed by ecgonine, its ethers or benzoylecgonine, whereas the ethers of benzoylecgonine (Falck, *Inaugural-Diss. Kiel*, 1886) and the ethers of derivatives of ecgonine containing other acid radicles, such as isatropyl, cinnamyl, phthalyl, phenylacetyl, &c., act on the liver in the same way as cocaïne itself. Of all these compounds, only the phenylacetic derivative is an anæsthetic, and the same relations hold for the *d*-cocaïnes.

Orthochloro- and metanitro-derivatives of both *l*- and *d*-cocaïne have but little anæsthetic action but produce the characteristic effect on the liver, whilst the metamido-compounds are devoid of both these properties. The metahydroxy-derivatives occupy an intermediate position, having a very slight anæsthetic action, and only producing the characteristic action on the liver in large doses. When the acetyl- or benzoyl-group is introduced into the amido-group of the amido-cocaïnes, the substances obtained act on the liver but are not anæsthetics, whilst the cocaïne-urethanes are much more powerful anæsthetics than cocaïne itself, and also have the characteristic action on the

liver. On the other hand, metabenzenesulphamido-*d*-cocaïne and *d*-cocaïnecarbamide have no anæsthetic effect, so that this property does not simply depend on the neutralisation of the basic amido-group by an acid radicle. The colouring matters derived from *d*-cocaïne have also been examined; *d*-cocaïneazodimethylaniline hydrochloride only produces extremely slight anæsthesia, whereas *d*-cocaïneazo-*α*-naphthylamine hydrochloride is an anæsthetic, but does not act on the liver. The norcocaïnes have a more powerful anæsthetic action than the cocaïnes themselves, and also act on the liver, but they are much more violent poisons.

The compounds of cocaïne with methylic iodide possess none of the characteristic physiological properties of the cocaïnes.

The power of producing anæsthesia is by no means confined to the alkaloïds of the cocaïne series, since it is common to many benzoyl and other derivatives of alkaloïds, which will form the subject of further communications.   A. H.

Chemistry of Vegetable Physiology and Agriculture.

Composition of Yeast. By P. GUICHARD (*Bull. Soc. Chim.*, [3], **11**, 230—239).—See this vol., ii, 395.

Constituents of the Nodes and Internodes of the Sugar Cane. By J. L. BEESON (*Amer. Chem. J.*, **16**, 457—464).—It being a belief among sugar planters that the nodes (joints) of the sugar cane are the main source of the reducing sugars contained in the expressed juice, the author has investigated the subject. The nodes and internodes of *a*, ripe growing canes, *b*, dead canes in varying stages of decay, and *c*, canes where the node-eyes were in different stages of development or germination were examined. The results obtained were as follows. The juice expressed from the nodes of the cane is quite different from that of the internodes. That from the nodes is highly coloured, gives a heavy precipitate with basic lead acetate, and a heavy coagulum on boiling ; that from the internodes is clear, light in colour, gives only a small precipitate with lead acetate, and no appreciable coagulum on boiling. The juice from the nodes contains markedly less (in ripe growing canes from about one-half to one-tenth) reducing sugars, more solids not sugars, and more coagulable substances. The fibre of the nodes contains more proteïds, and more insoluble carbohydrates not sugars, which readily pass into reducing sugars. As the cane deteriorates (decays), reducing sugars are formed more rapidly in the nodes than in the internodes, and probably glucose is the first visible product of plant assimilation by the young cane. The author believes that these facts can be best explained by the hypothesis that the physiological function of the node in the cane is similar to that of the seeds in flowering plants, namely, to store food in the region of the germinating eye for the

use of the young plant before it has taken sufficient hold of the earth to draw sustenance from the atmosphere and soil. This hypothesis is confirmed by the fact that the isolated nodes of the sugar cane when planted will germinate and grow to maturity. If this hypothesis is correct in the case of the cane, it may be true also in the case of other plants which propagate from the nodes. L. T. T.

Analytical Chemistry.

Detection of Hydrochloric acid. By A. VILLIERS and M. FAYOLLE (*Compt. rend.*, **118**, 1152—1154, and 1204—1206).—The method is based on the fact that, with an acid solution of aniline, iodine produces no apparent reaction, or yields a colourless, soluble, substitution derivative, bromine forms a white, insoluble, substitution derivative, whilst chlorine forms products which are black, and insoluble with a large proportion of the gas, and with a small proportion are violet-red when warm, and blue when cold, gradually changing to red.

The aniline solution whilst acid must not contain a large quantity of an inorganic acid. The following solution answers well, and can be kept unchanged for a long time in yellow glass flasks; colourless saturated aqueous solution of aniline, 400 c.c.; glacial acetic acid, 100 c.c.

The liquid, previously concentrated or diluted to 10 c.c., is placed in a small flask, and 5 c.c. of a mixture of equal volumes of sulphuric acid and water is added, and then 10 c.c. of a saturated solution of potassium permanganate. The flask is gently heated, and the gas evolved is passed into 3—5 c.c. of the aniline solution contained in a tube surrounded by cold water. The reaction will detect 0·001 gram, or even 0·0005 gram, of hydrochloric acid when mixed with 1000 parts of bromine or iodine, but the presence of a considerable quantity of bromine reduces the delicacy of the reaction, in consequence of the formation of bromine chloride.

In presence of bromine, the halogens are precipitated in the form of silver salts, and the precipitate is digested for some time with a mixture of 10 vols. of water and 1 vol. of ammonia solution. Silver iodide is not dissolved at all, silver bromide is dissolved only very slightly, whilst the silver chloride is dissolved more or less completely. The reduction of the filtered liquid by means of zinc or magnesium and an acid, does not give very satisfactory results, and it is best to expel the ammonia *completely* by boiling, and then add hydrogen sulphide. The filtrate is afterwards boiled and concentrated to 10 c.c.

Ordinary corks should not be used in the construction of the apparatus, and the oxidation should take place in a flask provided with a glass stopper, and with a delivery tube attached by fusion.

When cyanides are present, cyanogen chloride may be formed, but hydrocyanic acid is easily expelled by heating with dilute sulphuric acid. In the case of complex cyanides, the liquid must first be distilled with sulphuric acid until vapours of the latter begin to pass over, mixed with water, and again distilled, the two distillates being afterwards mixed, and concentrated by evaporation.

When the halogens are not precipitated as silver salts, ammonium salts, if present, may interfere, in consequence of their well known reaction with chlorine. Ammonium compounds can, however, easily be expelled. C. H. B.

Estimation of Sulphur in Pyrites. By T. S. GLADDING (*J. Amer. Chem. Soc.*, **16**, 398—404).—The author recommends the following process. 1 gram of the finely powdered and dried ore is introduced into a beaker and mixed with 10 c.c. of bromine solution (50 c.c. bromine, 78 grams potassium bromide, in 500 c.c. of water), and allowed to remain 10 minutes in the cold, when 10 c.c. of nitric acid is added. The beaker, which must have a glass cover on it, is put into a water-bath, which is then slowly heated to boiling; when solution is effected, the liquid is evaporated to dryness. The contents are moistened with 10 c.c. of hydrochloric acid, the cover is once more put on, and when violent action has ceased, the whole is evaporated to dryness once more; the residue is now moistened with 1 c.c. of hydrochloric acid, and then digested with 50 c.c. of hot water until completely dissolved. The filtrate is precipitated hot, with a slight excess of ammonia, the precipitated ferric hydroxide is washed six times with hot water, and the filtrate, after adding a slight excess of hydrochloric acid, is precipitated, while boiling, with barium chloride solution (10 per cent.).

The ferric hydroxide may retain a trace of sulphuric acid, but this may be recovered by dissolving it in dilute hydrochloric acid and precipitating with barium chloride. One filter will do for the two precipitates. L. DE K.

Colorimetric Estimation of Ammonia. By L. ILOSVAY DE NAGY ILOSVA (*Bull. Soc. Chim.*, [3], **11**, 216—226).—The author recommends the employment of Wolff's colorimeter for the estimation of small quantities of ammonia. Frommodorff's method is the best for the colorimetric determination of nitrous acid; the estimation of nitric and nitrous acids by reduction to ammonia by distillation with metallic iron, is only accurate if the iron is pure. Full directions for carrying out the various operations are given. W. J. P.

A Wet Method for Estimating Nitrogen in Nitrates and in Nitro- and Nitroso-Compounds. By M. KRÜGER (*Ber.*, **27**, 1633—1635).—0·2—0·3 gram of the substance to be analysed is mixed with 20 c.c. of water (or of alcohol, if it is insoluble in water), 10 c.c. of a strongly acid solution of stannous chloride in hydrochloric acid, and 1·5 gram of tin, best obtained by precipitating a solution of stannous chloride with zinc. The mixture is heated with a small flame until all colour has disappeared and the tin is entirely dissolved. It

is then cooled (or the alcohol, if any was used, is evaporated), treated
with 20 c.c. of strong sulphuric acid, and heated until copious fumes
of sulphuric acid are evolved. In the case of a nitrate, it is now only
necessary to make the solution alkaline and distil off the ammonia.
In the case of a nitro- or nitroso-compound, an amido-derivative will
now be present, and this must first be oxidised as described in this
vol., ii, 258 (where 0·2—0·8 is a misprint for 0·2—0·3 gram). The
results are accurate. If the substance is volatile with steam in acid
solution, it must be heated very gently on the water bath with the tin
and stannous chloride until the reduction is complete. It is even
better to carry out the reduction in a sealed tube at 100°.

C. F. B.

Estimation of very small Quantities of the Nitrogen acids.
By G. LUNGE and A. LWOFF (*Zeit. angw. Chem.*, 1894, 345—350).—
Estimation of Nitric acid.—This may be accurately effected by a colori-
metric test. 0·2 of brucine is dissolved in 100 c.c. of pure sulphuric
acid. 0·0721 gram of potassium nitrate is dissolved in 100 c.c. of
water and 10 c.c. of this is diluted to 100 c.c. with strong
sulphuric acid. 1 c.c. of the nitrate solution to be tested is mixed
with 1 c.c. of the brucine solution and diluted with sulphuric acid
to 50 c.c.; a red colour makes its appearance, but cannot be taken
advantage of. The contents are temporarily put into a beaker and
heated to 70—80°, which will change the colour to a permanent
greenish-yellow. Trial experiments are now made with the standard
nitrate solution, until the same tint is obtained, when the operation is
finished. Contrary to general belief, the reaction is not interfered
with by the presence of a nitrite.

Estimation of Nitrous acid in Commercial Sulphuric acid.—1 c.c. of
Griess's reagent is put into each of a pair of Nesslerizing tubes and
mixed with 40 c.c. of water and 5 grams of sodium acetate. To the
contents of the first tube 1 c.c. of the suspected acid is added and to
the other, without delay, 1 c.c. of a standard nitrite solution, prepared
by dissolving 0·0493 gram of pure sodium nitrite in 100 c.c. of water
and diluting 10 c.c. of this to 100 c.c. with pure sulphuric acid. The
reddish colours may be compared after any convenient time, but it is
best to wait five minutes.

The authors prepare Griess's reagent as follows:— 0·1 gram of
white *a* naphthylamine is boiled for 15 minutes with 100 c.c. of water
and mixed with 5 c.c. of glacial acetic acid. The solution is then
mixed with 1 gram of sulphanilic acid dissolved in 100 c.c. of water,
and the mixture preserved in a well corked bottle. If, in course of
time, it should become rather too red, it may be decolorised by
shaking it with zinc dust.   L. DE K.

Estimation of Phosphoric acid. By S. W. JOHNSON (*J. Amer.
Chem. Soc.*, **16**, 462—465).—The author states that although the
citrate method generally gives good results, this is only caused by a
fortunate compensation of errors, the magnesia precipitate being con-
taminated with lime and also with iron and alumina, whilst the filtrate
retains notable quantities of phosphoric acid.

As regards the molybdate precipitation, the process generally gives

results which are too high, and if an effort be made to prevent this by adding more nitric acid the results will be too low, unless the filtrate is further digested with more molybdate solution.   L. DE K.

Estimation of Silica in Blast Furnace Slag. By P. W. SHIMER (*J. Amer. Chem. Soc.*, **16**, 501—502).—The author points out that spinel is not decomposed by the usual alkali carbonate fusion, and remains in consequence with the silica. It is, therefore, never safe to omit the treatment of the weighed silica with sulphuric and hydrofluoric acids to ascertain its purity.

Spinel may be detected by repeatedly boiling slag with hydrochloric and hydrofluoric acids, followed up by boiling with sodium carbonate. It is then left behind as a crystalline powder.   L. DE K.

Sources of Error in Potash Estimations. By N. ROBINSON (*J. Amer. Chem. Soc.*, **16**, 364—372).—The determination of potash in commercial potash salts or fertilisers is, as yet, in a somewhat unsatisfactory state. The author points out a few sources of error. In the Lindo-Gladding process, for instance, error is introduced by the action of the solution of ammonium chloride on the precipitated potassium platinochloride, a slight double decomposition taking place, some potassium going into solution and a corresponding amount of ammonium passing into the precipitate.

In the Stassfürt or German method of analysis, the sulphates which are present are decomposed by means of barium chloride; the author calls attention to the large amount of potassium which is carried down, by occlusion, as he calls it, by the barium sulphate, and is not completely removed by washing.   L. DE K.

Electrolytic Analyses. By F. RÜDORFF (*Zeit. angw. Chem.*, 1894, 388—389).—The present paper (compare Abstr., 1893, ii, 305, 391) deals mainly with the separation of mercury from other metals.

Mercury from Cadmium.—The liquid is mixed with 2 c.c. of nitric acid (sp. gr. 1·2) and diluted to 120 c.c. It is then electrolysed with two Meidinger cells. If the cadmium largely preponderates, 5 c.c. of acid is added. After about eight hours, the mercury will have completely separated.

Mercury from Zinc.—The metals may be in the form of chlorides or nitrates. The neutral solution is mixed with 1 c.c. of nitric or 10 drops of sulphuric acid, diluted to 120 c.c., and electrolysed with two or three cells. If four cells be used, some zinc is also deposited.

Mercury from Iron.—The liquid is mixed with 4—5 drops of sulphuric acid, diluted to 120 c.c., and electrolysed with two or three cells.

Mercury from Nickel.—The liquid is mixed with 6 drops of sulphuric acid, diluted to 120 c.c., and electrolysed with two or three cells. The mercury is completely precipitated in the course of a night.

Mercury from Manganese.—The liquid is mixed with 3 drops of 10 per cent. sulphuric acid, diluted to 120 c.c., and electrolysed with two cells. The amount of manganese should not exceed 0·03 gram, otherwise it will not firmly adhere to the + electrode. It separates as hydrated manganese dioxide.   L. DE K.

Valuation of Zinc Dust. By O. BACH (*Zeit. angw. Chem.*, 1894, 291—292).—1 gram of the sample is placed in a flask containing a little water and a small cylinder filled with a sufficiency of sulphuric acid ; the flask is fitted with a doubly perforated india-rubber cork, through which pass two glass tubes bent at right angles, one of which reaches nearly to the bottom of the flask, and is in connection with a carbonic anhydride apparatus, whilst the other is connected with a delivery tube leading to a burette filled with, and standing over, 10 per cent. aqueous soda.   Carbonic anhydride is first passed until all the air has been expelled, and, after connecting the delivery tube with the burette, the sulphuric acid is made to run into the flask.   After the action has ceased, more carbonic anhydride is passed, until the volume of gas in the burette no longer increases ; the burette is transferred to a large cylinder filled with water, and, after levelling, the volume of hydrogen is read off and corrected for temperature and pressure.   The calculation may be avoided by using Dietrich's tables.   L. DE K.

Analyses of Zinc, Zinc Dust, Zinc Ores, &c. By F. MEYER (*Zeit. angw. Chem.*, 1894, 391—395).—*Estimation of Zinc in Ores.*— 0·5 gram of the dry, powdered sample is treated as usual with 10 c.c. of nitrohydrochloric acid, and after the excess of acid has been expelled by heat, the residue is taken up with 10 c.c. of bihydrated sulphuric acid and heated until sulphuric fumes appear, so as to separate the lead.   When cold, the mass is dissolved in 60—80 c.c. of hot water, and boiled with 10 c.c. of solution of sodium thiosulphate (1—8) to precipitate any copper, cadmium, &c.; after filtering, any iron is oxidised by adding 5 c.c. of nitric acid, and the liquid is boiled to better separate the sulphur.   Iron and alumina are now precipitated by the addition of 30 c.c. of ammonia, and, when cold, 20 c.c. of bromine water is added to remove any manganese.   The precipitate is collected, redissolved in acid, and reprecipitated with ammonia and bromine water to free it from zinc; the united filtrates are then made up to 500 c.c., and an aliquot part titrated with sodium sulphide (Schaffner's process).

The process is also applicable to the analysis of spelter, zinc fume, zinc dust, and zinc white.   Sulphur is best estimated by Lunge's process (oxidation by nitric acid and potassium chlorate, removal of iron by ammonia, and precipitation of the sulphuric acid by barium chloride).   L. DE K.

Analytical Properties of Iron Phosphide and Phosphate. By L. M. DENNIS and B. S. CUSHMAN (*J. Amer. Chem. Soc.*, 16, 477—485). —The authors prepared iron phosphide by decomposing ferrous chloride at a red heat by hydrogen phosphide.   Contrary to expectation, the product gave analytical results corresponding with the formula FeP, and not Fe_3P_4.   It has been proposed to effect the separation of iron phosphide from iron phosphate by means of a current of chlorine at a white heat, but, although this method behaves admirably for the simple substances, the authors found it quite

unsuited for an analysis of a mixture. Other methods of analysis were also found to be unsatisfactory. L. DE K.

Estimation of Nickel by means of Mercuric Ammonium Cyanide. By F. W. SCHMIDT (*Ber.*, **27**, 1624—1627; compare this vol., ii, 160).—The solution of nickel salt is mixed with ammonium nitrate in excess, and ammonia added until the liquid is coloured pale blue; it is then boiled, and the nickel precipitated with hydrogen sulphide solution in excess. The nickel sulphide may readily be collected on a filter, and is as stable in air as cupric sulphide. After washing with hydrogen sulphide solution, it is converted into oxide by the action of mercuric ammonium cyanide, in the manner previously described (*loc. cit.*). The results of determinations given in the paper, made by the author and others, agree closely with the theoretical. The action of ammonium nitrate in facilitating the precipitation of nickel sulphide is not unique, but is analogous to the action of other neutral salts, such as sodium chloride, potassium iodide, magnesium sulphate, &c., on the yellow solution of oxythioarsenious acid, or on the orange-red solution of thio- or oxythio-antimonious acid; these appear to be colloïdal solutions, which the neutral salts coagulate. The author's previous suggestion (*loc. cit.*), that mercuric ammonium cyanide would be found to decompose natural sulphides, is confirmed, so far as regards copper pyrites, which is quickly converted into a mixture of ferric and cupric oxides; the same result is attained by carefully roasting the finely-divided mineral in a porcelain crucible. J. B. T.

Separation of Titanium from Iron. By C. BASKERVILLE (*J. Amer. Chem. Soc.*, **16**, 427—428).—The separation of titanium from iron, by means of sulphurous acid, has been confined to their sulphates. The process is tedious, and often unsatisfactory.

The author has, however, found that the separation is rendered easy and accurate when the chlorides are acted on. Sulphates may be changed into chlorides by precipitating with ammonia and redissolving in hydrochloric acid, the excess of which is then again neutralised. L. DE K.

Estimation of Zirconium by means of Sulphurous acid. By C. BASKERVILLE (*J. Amer. Chem. Soc.*, **16**, 475—476).—The author has found that zirconium may be accurately estimated, and even quantitatively separated from iron and aluminium by boiling with sulphurous acid, but the reaction only succeeds when the metals exist as neutral chlorides. If, as usually happens, the salts exist as acid sulphates, these must be first converted into chlorides by precipitating with ammonia and carefully redissolving in hydrochloric acid. Iron is titrated in the filtrate from the zirconium. The test-analyses prove the great accuracy of the process. L. DE K.

Quantitative Analysis of Natural Gas. By F. C. PHILLIPS (*Amer. Chem. J.*, **16**, 412—416).—As in natural gases higher members of the paraffin series than methane may be present, the Bunsen

method of analysis is difficult, if not impossible. The author, in his work (this vol., ii, 387), has substituted with advantage combustion of the gases over copper oxide. After determining the carbonic anhydride, olefines, &c., in the usual way, a given volume of the residual gas is slowly passed from a graduated and specially arranged pipette, over red-hot copper oxide in a combustion tube, and the water and carbonic anhydride formed, are absorbed, and weighed in the usual way. Before combustion, the tube is washed out with pure nitrogen, and afterwards, first with nitrogen, and finally with air. The nitrogen is determined by a modification of the usual volumetric combustion method. In this way the volume of the paraffin and the weights and ratio of the contained carbon and hydrogen are determined. This gives some indication of the composition of the gaseous paraffins present, and valuable data are obtained for determining the heating value of the gas.   L. T. T.

The Iodine-Absorption of some of the Rarer Fatty Oils. By J. A. ROELOFSEN (*Amer. Chem. J.*, **16**, 467—469).—The iodine absorption figures for about 50 vegetable and animal oils (mostly rare, and previously undetermined) from trustworthy sources, were determined by the Hübl method, as described in Allen's "Commercial analysis," and the results and descriptions of the oils are given in the paper.   L. T. T.

Estimation of Rosin Oil in Mineral Oils. By P. C. McILHINEY (*J. Amer. Chem. Soc.*, **16**, 385—388).—After describing various published processes for effecting the separation, the author finally recommends the following method. 50 c.c. of nitric acid of 1·2 sp. gr. is heated to boiling in a 700 c.c. flask, and after removing the source of heat 5 grams of the suspected oil is added. The flask is then heated on the water-bath, with frequent shaking, for about 20 minutes, when about 400 c.c. of cold water is added. After cooling, the liquid is shaken with 50 c.c. of light petroleum, which dissolves the oil which has not been acted on. The liquid is now carefully poured off from the resinous matter into a separator, and, after settling, the aqueous portion is drawn off, and the petroleum poured into a tared flask. The flask containing the resin is rinsed out with some more light petroleum which is then also introduced in the tared flask. After distilling off the solvent, the oil is weighed. It must be remembered that even pure mineral oils lose about 10 per cent. of their weight by the nitric acid treatment. The test-analysis is very satisfactory.
                                                              L. DE K.

Estimation of Lecithin in Plants. By B. v. BITTO (*Zeit. physiol. Chem.*, **19**, 488—498).—If any vegetable tissue is extracted first with ether, and then twice with alcohol, each extraction lasting an hour, only a part of the lecithin goes into solution. It is necessary, after extraction with ether, to extract with boiling ethylic alcohol 30, or with methylic alcohol 20 times at least. Each extraction should last 8—10 minutes, never longer than a quarter of an hour.
                                                              W. D. H.

Alkaloïd-like Reactions of Acetanilide. By E. Schär (*Arch. Pharm.*, **232**, 249—261).—Many of the colour reactions of acetanilide are similar to those of the common alkaloïds; the author has made a comparative study of these, and tabulates his results for analytical purposes. W. J. P.

Estimation of Cystin. By P. Borissow (*Zeit. physiol. Chem.*, **19**, 511—520).—Breuzinger showed that cystin hydrochloride formed with mercuric chloride an almost insoluble crystalline compound. In the present research some experiments are recorded in which an attempt was made to estimate cystin in a similar way. In aqueous solutions, fairly good results were obtained, if a number of precautions are observed, which are fully described. In urine, however, the difficulties do not appear to have been satisfactorily overcome; the experiments made are described in full. W. D. H.

Estimation of Nicotine in Tobacco. By G. Heut (*Arch. Pharm.*, **231**, 658—663).—Having reviewed the methods which have been suggested for the estimation of nicotine in tobacco (Abstr., 1892, 771; 1893, ii, 504), the author concludes that Kissling's method (compare Vedròdi) is the most generally applicable. By adopting Pezzolata's method for separating nicotine and ammonia (Abstr., 1893, ii, 504), he has proved that when anhydrous ether is employed in Kissling's method, a distillate which is free from ammonia is obtained.

Pezzolata's suggestion that magnesia should be used as the base for the liberation of the nicotine was found to be valueless in the author's hands. It is pointed out that not only does ammonium sulphate partially dissociate during the evaporation in Pezzolata's method, but also the nicotine sulphate. Acid nicotine sulphate is, however, free from this fault, so that care must be taken that the base is converted into the acid salt. A. G. B.

Rapid Titration of Xantho-uric Compounds in Urine. By G. Denigès (*Bull. Soc. Chim.*, [3], **11**, 226—230).—The xantho-uric compounds (uric acid, xanthine, &c.) in urine are usually determined by Haycraft's method, which consists in adding ammoniacal silver nitrate and sodium hydrogen carbonate or a magnesium salt, and determining the amount of silver in the precipitate. The complete filtration of the silver salt is, however, a very long process; the author therefore determines the silver remaining in an aliquot part of the filtrate, and thence deduces the amount of silver precipitated.

A solution (A) is made by dissolving 150 grams of ammonium chloride and 100 grams of magnesium chloride per litre in strong ammonia, and mixing the resulting solution with an equal volume of decinormal silver nitrate solution. Another solution (B) contains 10 grams of pure potassium cyanide and 10 c.c. of strong ammonia, in 500 c.c. of water; it is standardised by the usual process. The titration of the urine is carried out by adding to 100 c.c., 25 c.c. of solution A; the liquid is then filtered, and 20 c.c. of solution B, and a few drops of 20 per cent. potassium iodide solution containing 2 per cent.

of ammonia are added to 100 c.c. of the filtrate. The liquid is then titrated with N/10 silver nitrate solution, until a persistent turbidity is obtained. From the results, the quantity of xantho-uric compounds present may be readily calculated as uric acid. The process is applicable to urines containing albumin, but any iodide present must be removed by adding 1 c.c. of nitric acid and 20 c.c. of N/10 silver nitrate to 100 c.c. of the urine; the excess of silver nitrate is then precipitated by sodium chloride, the solution made up to 200 c.c. with water, and filtered. The uric acid is then determined in 100 c.c. of the filtrate by the process described above.

Test analyses gave very good results.   W. J. P.

Composition and Analysis of Yeast. By P. GUICHARD (*Bull. Soc. Chim.*, [3], **11**, 230—239).—The author gives a summary of analyses of yeast made by various chemists.

Recently pressed yeast always loses about 72 per cent. of water at 120°, or by standing over sulphuric acid or calcium chloride; as it dries, the yeast loses its fermentative properties, but regains them under favourable conditions. The density of the yeast cells is about 1·181 at 16°, and was determined by shaking with a mixture of alcohol and chloroform, and adding one or other liquid until the yeast neither rose nor sank. Light petroleum extracts 1·4 per cent. of fatty matter from the dried yeast, which also contains 6·7—7·2 per cent. of ash. The author describes a new apparatus for determining the fermentative power of yeast.   W. J. P.

General and Physical Chemistry.

Influence of Position-Isomerism on the Rotatory Power of Optically Active Compounds. By H. GOLDSCHMIDT and S. FREUND (*Zeit. physikal Chem.*, **14**, 394—408).—The molecular rotatory power was determined for a number of isomeric compounds, chiefly derivatives of phenylcarbamic acid, and of dextrorotatory carvoxime. The results are contained in the accompanying table.

Compound.	Specific rotation.	Mol. rotation.
Amylic phenylcarbamate, $CHMeEt\cdot O\cdot CO\cdot NH\cdot C_6H_5$	$+ 4\cdot19°$	$+ 8\cdot67°$
Amylic orthotolylcarbamate, $CHMeEt\cdot O\cdot CO\cdot NH\cdot C_7H_7$......	$+ 2\cdot66$	$+ 5\cdot88$
Amylic metatolylcarbamate, ,, ...	$+ 3\cdot85$	$+ 8\cdot51$
Amylic paratolylcarbamate, ,, ...	$+ 4\cdot47$	$+ 9\cdot88$
Menthylic phenylcarbamate, $C_{10}H_{19}\cdot O\cdot CO\cdot NH\cdot C_6H_5$.........	$-77\cdot21$	$-212\cdot33$
Menthylic orthotolylcarbamate, $C_{10}H_{19}\cdot O\cdot CO\cdot NH\cdot C_7H_7$	$-65\cdot88$	$-190\cdot39$
Menthylic metatolylcarbamate, ,, ...	$-71\cdot43$	$-206\cdot44$
Menthylic paratolylcarbamate, ,, ...	$-72\cdot30$	$-208\cdot94$
Carbanilidocarvoxime, $C_{10}H_{14}\cdot NO\cdot CO\cdot NH\cdot C_6H_5$	$+31\cdot67$	$+ 89\cdot94$
Carborthotoluidocarvoxime, $C_{10}H_{14}\cdot NO\cdot CO\cdot NH\cdot C_7H_7$........	$+27\cdot40$	$+ 81\cdot65$
Carbometatoluidocarvoxime, ,, ...	$+29\cdot79$	$+ 88\cdot77$
Carboparatoluidocarvoxime, ,, ...	$+30\cdot75$	$+ 91\cdot64$
Benzoylcarvoxime, $C_{10}H_{14}\cdot NO\cdot CO\cdot C_6H_5$..................	$+26\cdot64$	$+ 71\cdot66$
Orthotoluylcarvoxime, ,, ...	$+27\cdot08$	$+ 76\cdot64$
Metatoluylcarvoxime, ,, ...	$+26\cdot86$	$+ 76\cdot01$
Paratoluylcarvoxime, ,, ...	$+23\cdot44$	$+ 66\cdot34$
Phenacetylcarvoxime, ,, ...	$+40\cdot63$	$+114\cdot98$
Orthobromobenzoylcarvoxime, $C_{10}H_{14}NO\cdot CO\cdot C_6H_4Br$	$+25\cdot96$	$+ 90\cdot34$
Metabromobenzoylcarvoxime, ,, ...	$+18\cdot24$	$+ 63\cdot48$
Parabromobenzoylcarvoxime, ,, ...	$+14\cdot90$	$+ 51\cdot85$
Orthonitrobenzoylcarvoxime, $C_{10}H_{14}\cdot NO\cdot CO\cdot C_6H_4\cdot NO_2$......	$\pm 0\cdot0$	$\pm 0\cdot0$
Metanitrobenzoylcarvoxime, ,, ...	$+20\cdot68$	$+ 64\cdot94$
Paranitrobenzoylcarvoxime, ,, ...	$+17\cdot33$	$+ 54\cdot42$

It is noticeable that in most cases the value of the meta-compound falls between those of the ortho- and para-compounds, and that in the three last series of compounds the difference between the values of the meta- and para-compounds is approximately constant, namely 3·42; 3·34; 3·45 (*i.e.* for specific rotation).   L. M. J.

An Electrode Sensitive to Light. By H. LUGGIN (*Zeit. physical Chem.*, **14**, 385—393).—The author describes a form of electrode considerably more sensitive to light than any employed by previous investigators and gives a few details of its construction. It consists of a platinum plate covered with bromide of silver, and, when used, is paired with a similarly coated silver electrode in a decinormal solution of potassium bromide. The rise of potential is determined by a quadrant electrometer, and in some experiments

exposure to diffused daylight caused an increase of potential of 0·42 volt. The experiments show that when illuminated by weak light the rate of rise of potential is uniform and represented by a straight line until a maximum value is reached, after which it remains constant, or may fall slightly. With a stronger light, the rate of increase is more rapid, but the final value is not greater, the rate, however, is not directly proportional to the intensity of the light, but is proportionally less than for weak lights, whilst it is also lowered by previous exposure to a powerful light. Continuous and intermittent lights of the same mean intensity appear to have the same effect. The sensitiveness of the plate, however, does not remain constant, but, even after long rests, very different potential-increases are obtained with the same light.   L. M. J.

Electrolysis and Polarisation of Mixtures of Salts. By L. HOULLEVIGUE (*Ann. Chim. Phys.*, [7], **2**, 351—384).—According to Buff, when a mixture of two salts is electrolysed there is always a fixed ratio between the amounts of each decomposed by the current, and this ratio is independent of the strength of the current used. In a former paper (Abstr., 1890, 678) the author has shown that Buff's law is not strictly true, but is complicated by the probable occurrence of secondary actions, and further that if the secondary action is supposed to be proportional to the time, the ratio should be a hyperbolic function of the intensity of the current. In the present paper, it is shown that in the electrolysis of mixtures of zinc and copper sulphates the ratio Zn : Cu deposited does actually increase with the current and is a hyperbolic function of the intensity. Buff's law is therefore only approximately true when the intensity of the current is sufficiently great.

In the electrolysis of mixtures of variable composition, it is found that the weight decomposed of the more readily electrolysable constituent increases regularly with the amount in which it is added to the mixture, except when the total amount present is very small. Thus, if to a fixed amount of zinc sulphate, copper sulphate is added in amounts which increase in arithmetical progression, and the mixtures are electrolysed under comparable conditions, the weight of copper deposited also increases in arithmetical progression.

The polarisation produced in a mixture of two salts depends on the nature of the constituents, even when only one of them would undergo electrolysis. It diminishes in proportion to the weight of the more electrolysable constituent introduced into the mixture, except when the actual amount present is but small. Lippmann's law of the depolarisation of an electrode placed in a mixture containing one of its own salts only holds for very small currents.

The author shows that there is a theoretical relationship between the nature of the deposits produced by electrolysis and the corresponding polarisation.   H. C.

Electrical Conductivity of Formic Acid. By V. SAPOJNIKOFF (*J. Russ. Chem. Soc.*, **25**, 626—631).—The electrical resistance of pure formic acid as determined by Hartwig appeared much too small

and was attributed by the author to the presence of considerable quantities of water in the acid. He therefore attempted to remove these as completely as possible, but found that, by recrystallisation, he could not obtain an acid melting above 8·4°. The conductivity of this acid, however, although it still contained traces of water, was only one-sixteenth of the conductivity of Hartwig's acid, namely 0.4×10^{-8} at 18·8°.   J. W.

Constitution of Inorganic Compounds. By A. WERNER and A. MIOLATI (*Zeit. physikal. Chem.*, **14**, 506—521).—The molecular conductivity of complex inorganic compounds, chiefly the double compounds of ammonia with salts of platinum, cobalt, &c., is employed as a means for elucidating their constitution. The salts may be divided into four groups, namely those in which the complex group is united with one, two, three, or four univalent ions respectively. The molecular conductivity (M_{1000}) for the members of those groups which were examined gave the following results :—(i) 96·7—108·5, (ii) 234·4—267·6, (iii) 383·8—426·9, (iv) 522·9 (only one examined). The variation is greatest in the higher groups owing to less simple splitting into ions, but the difference between members of different groups is well marked, that is, about 140. The molecular conductivities of a large number of compounds are recorded and in a few cases depicted graphically. Changes in constitution, such as from purpureo- to roseo-salts, &c., by absorption of water, are indicated by increase in the conductivity, more or less rapid, according to the rate of hydration. The author then points out that dichrocobalt chloride (this vol., ii, 51) has a molecular conductivity at 1° of 108·1, and must, therefore, be regarded as containing one chlorine ion, not three, as Jorgensen considered, but that, on standing, the compound passed by hydration into the compound with three chlorine ions. The effect of the substitution of water for ammonia in these classes of salts is also considered, and a table given. (Abstr., 1893, ii, 507.)
                                                                L. M. J.

Determination of Transition Temperatures. By E. COHEN and G. BREDIG (*Zeit. physikal. Chem.*, **14**, 535—547).—The method described by Cohen (Abstr., 1894, ii, 340) is frequently inapplicable, owing to one of the saturated solutions becoming super-cooled and not changing at the transition temperature. A slight alteration in the apparatus is therefore made, so that instead of two saturated solutions, one only is employed, the other electrode being immersed in an unsaturated solution of the compound. At the transition temperature there must be a sudden change in the temperature co-efficient of the electromotive force, that is, in the value of $\dfrac{dE}{dT}$. The apparatus employed is fully described, and experiments made with sodium sulphate are recorded. Curves are plotted with electromotive force as ordinate, and temperatures as abscissæ, and in each case sudden breaks are seen at the temperatures (1) 33·8°, (2) 33·0°, and (3) 32·9° respectively, the mean, 33·2°, agreeing satisfactorily with Cohen's previous determination, 32·8°, and with those of other

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observers by other methods. The value of $\dfrac{dE_2}{dT} - \dfrac{dE_1}{dT}$ is also calculated according to the equation $\dfrac{dE_2}{dT} - \dfrac{dE_1}{dT} = \dfrac{W_2 - W_1}{T_0} \cdot \dfrac{nb_0}{2(b_0 - 10)}$, where W_2 and W_1 are the heats of solution above and below T_0, n the migration rate of the sodium ion, and b_0 the number of molecules of water per molecule of the salt. Where two saturated solutions were employed, the value $\dfrac{dE}{dT}$ has also the same value, and in both cases the calculated and observed result agreed well, thus—calculated $1\cdot2$; $\dfrac{dE_2}{dT} - \dfrac{dE_1}{dT} = 1\cdot3$. $\dfrac{dE}{dT} = -1\cdot5$ millivolts. L. M. J.

Modifications of Beckmann's Ebullioscopic Apparatus. By C. E. LINEBARGER (*Chem. News*, **69**, 279—280).—To obviate the difficulties hitherto experienced when introducing the substance into the boiling solvent in the Beckmann ebullioscopic tube, the author does away with the side tube, fuses a piece of wider tubing on to the mouth, and fits this with a cork to take the thermometer and the end of the condensing tube, which is only 190 mm. long and 12 mm. in diameter, and being set upright, permits of any substance being dropped into the boiling solvent without risk of adherence to the sides. To minimise any escape of solvent during an experiment, the author suspends a small gilded copper surface condenser in the condensing tube, or closes the top of the latter with a cork carrying a small tube closed below and terminating above the cork with a capillary; in this tube some of the solvent is placed, and in the side of the tube, just above the liquid and below the cork, is a small perforation, so that any vapour escaping condensation has to pass by the perforation through this tube and capillary, before reaching the open air, and is therefore effectually condensed by the atmosphere already saturated with the vapour, and overflowing through the perforation is returned to the solution. D. A. L.

Thermodynamical Derivation of the Law of Van der Waals. By G. BAKKER (*Zeit. physikal. Chem.*, **14**, 456—466).—The author starts with three axiomatic propositions, namely, (1) that however high the temperature, the deviations from Boyle's and Gay Lussac's laws are finite; (2) that two fluid elements attract one another with a force which at any given temperature is dependent only on the masses and distances, and decreases rapidly as the distance increases; (3) the kinetic energy is a function of temperature. Employing then the equation $T\left(\dfrac{dp}{dT}\right)_v - p = \left(\dfrac{de}{dv}\right)_r$, he deduces first the expression $p = T(fv) - \dfrac{a}{b^2}$, and hence when the density is small, $p = \dfrac{RT}{v - b} + \dfrac{a}{b^2}$. L. M. J.

Specific Gravity of Aqueous Solutions. By D. TURBABA (*Trav. Phys.-Chim. Soc. Sci. exper. Kharkoff*, 1893, Supp. 5, 1—315. In

Russian).—The author has made a series of specific gravity determinations with aqueous solutions of chloral hydrate, formic acid, acetic acid, propylic alcohol, and isopropylic alcohol. Pyknometers of capacities varying between 16 and 45 c.c. were employed, and a set of determinations was made in each case at 0°, 15°, and 30°, all numbers being referred to water at 4°. The author estimates his greatest error in the density to be $\pm$ 0·00008 to 0·00009. The results obtained, when treated by the arithmetical and graphical methods of Mendeléeff and Pickering, indicate breaks corresponding with hydrates of definite composition, which show a general agreement with the hydrates found by other observers, although there occur many exceptions in detail. For example, while Pickering finds from the freezing points of solutions of propylic alcohol hydrates with 0·5, 1, 2, 7, 17, and 42 mols. H_2O to 1 mol. C_3H_8O, the author obtains hydrates with 2, 6, 18, and 36 mols. H_2O from a consideration of the specific gravity. J. W.

Determination of Vapour Densities; Production of a Vacuum. By C. SCHALL (*J. pr. Chem.*, [2], **50**, 87—88).—An improvement in the apparatus already figured and described (Abstr., 1892, 553) is here depicted. The acid is now supplied to the cabonate in K (*loc. cit.*) through a stop-cock funnel sealed through the glass. The tube containing the substance whose vapour density is to be determined (D, *loc. cit.*) is attached to a small wire hook passing through a cork in the tube from the bulb; for this purpose, the said tube is not curved over as previously shown, but has a side tube sealed to it which serves for attachment to the vacuum pump.

To produce a vacuum without a mercury or water pump, the author passes the end of the tube (closed by a piece of rubber tube having a Bunsen valve in it) through which the exhaustion is to be effected, into a flask in which water can be boiled to expel the air, and which can then be closed so as to allow of the production of a vacuum by condensation. A. G. B.

The Volume Changes of Acids and Bases on Neutralisation. By E. RUPPIN (*Zeit. physikal. Chem.*, **14**, 467—485).—The author has investigated the volume changes when solutions of acids and bases are added in equivalent proportions, employing for the purpose Ostwald's modified form of Sprengel's pyknometer and using semi-normal solutions of the compounds employed. These consisted of the following acids:—Hydrochloric, nitric, chloric, iodic, perchloric, permanganic, acetic, ethylsulphuric, benzenesulphonic, methenedisulphonic, thiosulphuric, sulphuric, and hydroplatinochloric, with the bases, ammonium, lithium, sodium, potassium, thallium, tetramethylammonium, tetramethylphosphonium, trimethylsulphonium, barium, strontium, and calcium hydroxides. In all cases, except when ammonium hydroxide was employed, the volume change was positive, and in all cases the agreement with Ostwald's law was satisfactory, that is, the difference betweeen the changes of volume given by different acids with the same base had nearly the same value for all bases, and similarly for bases and an acid, the slight dis-

crepancies being due to incomplete dissociation. Tables are also given showing the differences in the volume change between ammonium and the other hydroxides with the various acids, and between acetic and the other acids with the various bases, this change being shown as an additive property of the ions present in the mixed solutions (see Abstr., 1893, ii, 417). L. M. J.

Influence of Pressure on the Properties of Solutions. By G. TAMMANN (*Zeit. physikal. Chem.*, **14**, 433—445).—Regarding the internal pressure of a solution to be given by the equation $\pi = K + \Delta K + p$, where K is the internal pressure of the solvent at zero external pressure, and p is the external pressure, the author points out that the alteration of physical properties may be connected with that of the internal pressure by the equation $\Delta E = f(\Delta K + p)$, and hence by the observation of the influence of external pressure on any property of a solution, the difference between the internal pressures of the solution and solvent may be determined. Finks' experiments on the influence of pressure on the electrical conductivity afford the necessary data, and from his results the values of ΔK for sodium chloride, hydrogen chloride, and zinc sulphate solutions are determined and compared with those obtained from the isobar diagrams. The concordance is not very good, but is sufficient to justify the reasoning, especially in view of the magnitude of the probable errors. The corrections of the conductivity for internal pressure are given in the case of the same three salts, and the paper concludes with a short inquiry into the cause of the alteration in conductivity by pressure. It may be due to a change (1) in the number of free ions, or (2) in the internal friction between the ions and molecules of the solvent and dissolved substance. The second of these he considers the chief cause, as Röntgen's experiments show that in the case of water a pressure of 500 atmospheres has very little influence on the number of free ions. The author considers that Röntgen's conclusions, which are the reverse of these, are not justified by his experiments. In the case of water, unlike that of other liquids, the friction diminishes with increased pressure, and hence the conductivity increases, whilst the reverse must obtain with other liquids (see also this vol., ii, 224, 268, 342). L. M. J.

Osmotic Pressure of Solutions of Finite Concentration. By T. EWAN (*Zeit. physikal. Chem.*, **14**, 409—423).—The equation $PV = RT$, as applied to solution, is not absolutely correct, owing to the omission of many factors, one of the most important being the heat of dilution of the solution. The author calculates the relations between osmotic pressure, &c., when this is taken into account, employing, as a fundamental equation, Kirchhoff's relation between the heat of dilution and the vapour pressure $-\dfrac{dQ}{dw} = \dfrac{RT^2}{JM_0} \dfrac{d}{dt} \log \dfrac{p_0}{p}$, where Q is the heat of solution of 1 gram of the salt in w grams of water at T degrees absolute temperature, J is Joules' equivalent, and p_0 and p are the vapour pressures of the solvent and solution respectively. An expression is first deduced connecting the vapour pressure

of the solution with its freezing point and heat of dilution, and the results are verified by means of sulphuric acid solutions (w varying from 1·826 to 16·825), the agreement between the observed and calculated results being entirely satisfactory. As in the expression, log p_0/p is not independent of the temperature, it follows that v. Babo's law is only valid when the heat of dilution is zero. An equation connecting the osmotic pressure and temperature is next deduced, which, by omitting terms of small value, reduces to $\dfrac{dP}{dt} =$ constant; that is, it is analogous to Ramsay and Young's gaseous formula $p = bT + a$. The effect of concentration is considered, and on the supposition that the equation should be of the form of that of Van der Waals, an expression is deduced $- P(v-b) = RT + JM\dfrac{dQ}{dw}$. The values of the heat of dilution of various solutions of cane-sugar are finally calculated from the lowering of the freezing point, but the observed and calculated values do not show very good agreement.

<div align="right">L. M. J.</div>

Determination of the Molecular Weight of Soluble Compounds by means of Red Blood Corpuscles. By W. Löb (*Zeit. physikal. Chem.*, **14**, 424—432).—A small quantity of the blood corpuscles are added to a solution of the salt or other compound contained in a small flask, which is then rapidly rotated for about three minutes, and the colour of the clear supernatant liquid noted. Two solutions are finally obtained of such strength that one is just coloured and the other not coloured, and the arithmetical mean is taken as that isotonic with the blood corpuscles. An estimation is similarly made with a solution of a salt of known molecular weight, and from this the required weight is obtained by the equation $m = p\,\dfrac{cM}{PC}$, where pP, cC, and mM are the concentrations, isotonic coefficients, and molecular weights of the two compounds. The following isotonic coefficients are employed. Organic compounds as sugar, &c., $c = 2$, and in salts the acid = 2, an alkali atom = 1, alkaline earth = 0. Details of the mode of preservation of the blood corpuscles are given, and the experimental results appended show that the method is one of considerable accuracy. It is available, however, only in the case of soluble compounds, and cannot be used for acids or bases; its advantage, when available, being the facility and rapidity of execution.

<div align="right">L. M. J.</div>

Historical Note on Isomorphism. By J. H. van't Hoff (*Zeit. physikal. Chem.*, **14**, 548).—The author points out, in connection with Retger's recently published papers on isomorphism (this vol., ii, 348, and previous abstracts), that Buys-Ballot in 1846 (*Ann. Phys. Chem.*, **67**, 433) drew attention to the fact that the chemical simplicity of a chemical compound was connected with the symmetry of its crystalline form, and adds a table by which this is clearly indicated.

<div align="right">L. M. J.</div>

Researches on Gas Reactions. By M. v. RECKLINGHAUSEN (*Zeit. physikal. Chem.*, **14**, 491—505).—The researches had for their object the volume alterations which occur during the reactions of gases, and the author in the first part of the paper describes the apparatus and methods employed for the purpose. By means of a style moving upon a rotating drum, the volume changes are directly recorded as a curve, with volume ordinates and time abscissæ. The gas mixtures employed were (1) hydrogen and chlorine; (2) carbonic oxide and chlorine; (3) ethylene and chlorine, of which the first two mixtures are sensitive to light, the third being unaffected by it. All the experiments were performed in diffused daylight, and the following results were obtained.

The mixture of hydrogen and chlorine expands at the moment of illumination, and this expansion then decreases, at first rapidly, then more slowly, until the original volume is reached, when the end of the action is indicated, and the whole mixture has been converted into hydrogen chloride. The expansion also diminishes before the end of the action, even if the mixture is protected from light; and the author considers it probable that the action continues in the dark. The second mixture behaves in a similar manner, but the final volume is only half the original. The third mixture, which is not sensitive to light, reacts, when suddenly mixed, without any initial expansion, which thus appears to be characteristic of the sensitive mixtures. He points out that the results differ from those of Bunsen and Roscoe, who observed no initial expansion, but leaves to further research the explanation of the difference. L. M. J

Velocity of Action in Non-Homogeneous Systems; Decomposition of Sulphuryl Chloride. By G. CARRARA and I. ZOPPELLARI (*Gazzetta*, **24**, i, 364—370).—The velocity of interaction of sulphuryl chloride and water was studied by placing a layer of the chloride in a small beaker, pouring water on it, and suspending the whole in a larger vessel containing water; the contents of both vessels were kept stirred by means of a current of air, and samples were withdrawn for analysis from time to time. The results show that the action occurring in this non-homogeneous system is of the first order and obeys the same laws as actions of the same order in a homogeneous system. The velocity of action remains the same when decinormal potash is substituted for the water, thus indicating that the sulphuryl chloride is decomposed by the water, and not by the alkali. W. J. P.

Inorganic Chemistry.

Nitramide. By J. Thiele and A. Lachman (*Ber.*, **27**, 1909—1910).—The authors have recently shown that urethane may be readily converted into nitrourethane, $NO_2 \cdot NH \cdot COOEt$ (this vol., i, 399). On the addition of potash dissolved in methylic alcohol to

a concentrated aqueous solution of this substance at $0°$, *potassium nitrocarbamate*, $NO_2 \cdot NK \cdot COOK$, separates in plates which are immediately decomposed by water with development of heat, yielding nitrous oxide and potassium carbonate. If, however, the salt is added to a mixture of ice and sulphuric acid, *nitrocarbamic acid* is set free, but at once splits up into carbonic anhydride and *nitramide*, $NO_2 \cdot NH_2$. To isolate the latter, the solution is saturated with ammonium sulphate and extracted with ether; on evaporating the ether in a current of air at the ordinary temperature, the nitramide crystallises out in prisms; it may also be obtained in lustrous plates by adding light petroleum to the ethereal solution. It melts at $72°$, but the melting point is considerably lowered by traces of moisture.

Nitramide is somewhat volatile at the ordinary temperature, and dissolves in all the common solvents with the exception of light petroleum, the aqueous solution having a strongly acid reaction. It is most unstable, and when mixed with copper oxide, lead chromate, or even glass powder, decomposes into nitrous oxide and water with development of heat. It is also decomposed by concentrated sulphuric acid and by hot water, but, unlike the alkylnitramines, is equally unstable in alkaline solutions. On reduction, it yields a substance having strong reducing properties, probably hydrazine.

H. G. C

Gaseous Nitrogen Trioxide. By G. I. PORSHNEFF (*J. Russ. Chem. Soc.*, **25**, 684—685).—From experiments, which are mostly confirmatory of older data, the author concludes that pure, dry nitrogen trioxide is incapable of existence in the gaseous state, the liquid substance on vaporisation decomposing into nitric oxide and nitrogen peroxide.

J. W.

Chlorinated Boracites. By G. ROUSSEAU and H. ALLAIRE (*Compt. rend.*, **118**, 1255—1257).—The authors have prepared chlorinated boracites of the metals of the magnesium group by the method previously employed for the preparation of iron chloroboracite. The products contain from 0.8 to 1.2 per cent. of calcium, and with a view to avoid the presence of this metal, borax was used in place of boronatrocalcite, but, except in the case of zinc, the results were unsatisfactory. The wet and dry methods used by Heintz and by de Gramont for the reproduction of boracite also gave negative results, except in the case of zinc. The chloroborates are not obtained by the action of the vapours of the metallic chlorides on the corresponding boracites, which seems to show that the efficiency of boronatrocalcite is due to the sodium borate which it contains, this being converted into sodium chloride, which acts as a mineralising agent. This view is supported by the fact that pure calcium borate and boronatrocalcite, from which the sodium compound has been removed by washing, do not yield chloroborates.

All the substituted borates obtained crystallise in cubes, tetrahedra, and dodecahedra, have a pseudo-cubic symmetry, but act on polarised light. Fouqué finds that the crystals are composed of aggregations identical in character with those of natural boracites.

The general formula of the chloroborates is $6M''O, 8B_2O_3, M''Cl_2,$

The zinc compound crystallises in colourless tetrahedra and rhomboidal dodecahedra of sp. gr. 3·48 ; it is very stable, and is formed under a variety of conditions. It is obtained (1) by the action of zinc chloride vapour on borax at a dull red heat, (2) by adding boric acid and a small quantity of borax to a fused mixture of zinc and sodium chlorides, and (3) by the wet process of Heintz and de Gramont.

The cadmium, nickel, and cobalt compounds are prepared by passing dry chlorine over an intimate mixture of boronatrocalcite and the finely-divided metal, heated to redness. The cadmium compound is colourless, and crystallises chiefly in cubes, with some tetrahedra and cubo-octahedra ; the nickel compound forms yellow tetrahedra and dodecahedra ; the cobalt compound forms tetrahedra and cubes, violet by reflected, and green by transmitted light.

The manganese compound is obtained in white cubes by the action of chlorine on a mixture of boronatrocalcite and manganese carbide, the product being purified by treatment with concentrated hydrochloric acid, and any carbon being separated by means of bromoform and methylenic iodide.

The method which yields the substituted boracites gives much less satisfactory results when applied to the artificial production of ordinary boracite.   C. H. B.

Silicon Compounds. By L. GATTERMANN and K. WEINLIG (*Ber.*, **27**, 1943—1948).—Gattermann (Abstr., 1889, 342) has described a method whereby compounds of silicon are obtained from silicon prepared by reducing silica with magnesium powder. The production of these compounds depends on the temperature at which the action is allowed to take place ; and in the present paper the authors specify the temperatures more carefully. A very convenient tube furnace is described in the original paper.

Silicon tetrachloride is obtained by the action of chlorine at 300—310°.

Silicochloroform is obtained by the action of hydrogen chloride at 450—500°.

Silicon hexachloride, Si_2Cl_6, is obtained from the crude silicon tetrachloride by fractional distillation ; the yield amounts to 10 grams of Si_2Cl_6 from 50 grams of crude chloride. It boils at 145—146°, and crystallises in large leaflets at −1°. When treated with dilute ammonia, it yields hydrogen and gelatinous silica. When the hexachloride is treated with chlorobenzene and sodium, silicontetraphenyl (m. p. 231°) is formed, and not siliconhexaphenyl. Since silicochloroform, under the same conditions, also yields silicontetraphenyl, it appears that in the silicon series there is a great tendency to form tetra-derivatives.

Silico-oxalic acid, $(SiOOH·SiOOH)_x$, is obtained as follows. The pure hexachloride is exposed in a platinum dish, cooled with ice, to the moisture of the air until it is converted into a solid, white mass. It is then allowed to remain over lime as long as hydrogen chloride is given off. The product contains 97 per cent. of silico-oxalic acid. When heated in a test tube, it decomposes violently with a feeble detonation. It also explodes when rubbed with a hard substance.

Silicon octochloride, Si_3Cl_8, is obtained from the residue of the fractional distillation of the hexachloride. It boils at 210—215°, has a vapour density corresponding with the formula Si_3Cl_8, does not solidify at $-12°$, and is rapidly decomposed by water to form an insoluble acid, which is probably *silicomesoxalic acid*,

$$(SiOOH \cdot SiO \cdot SiOOH)_x.$$

This has strong reducing properties, and explodes much more violently than silico-oxalic acid. E. C. R.

Properties of Graphite obtained from Various Metals. By H. N. WARREN (*Chem. News*, **69**, 291).—Compared with graphite from iron, graphite obtained from nickel and cobalt is much finer; from ferro-manganese it is in thinner scales, less readily oxidised and brownish in colour; from manganese it is in still larger scales, distinctly brown, frequently translucent, and still less readily oxidised; from "chrome-eisen" the scales are much harder and brighter; from chromium they are more like silicon, with a semi-metallic lustre, and are oxidised with great difficulty. The character of the graphite depends, however, on the character of the fusion of the various metals; the varieties are, moreover, inter-convertible; thus, on introducing into molten iron, graphite from manganese, it acquires the properties of graphite from iron. D. A. L.

Refraction Constants of Organo-metallic Compounds. Atomic Refractions of the Elements. By A. GHIRA (*Gazetta*, **24**, i, 309—324; 324—327).—The author has determined the refraction constants of a number of organo-metallic compounds for the rays $H\alpha$, $H\beta$, $H\gamma$, and D, and from the results has calculated the atomic refractions of the metals. The results for the line $H\alpha$ are tabulated below.

Substance.	Temperature.	$P\dfrac{\mu_{H_\alpha} - 1}{d}$	$P\dfrac{\mu_{H_\alpha}^2 - 1}{(\mu_{H_\alpha}^2 + 2)d}$	Atomic refractions of the metals.	
				From μ.	From μ^2.
HgMe₂	22·2°	41·09	23·96	23·29	12·76
HgEt₂........	23·2	56·97	33·13	23·97	12·81
HgPh₂	22·7	114·20	64·39	26·80	13·55
HgNO₃.......	10·3	36·0	20·5	20·72	11·66
SbCl₃........	16·4	53·09	32·24	23·69	14·18
,, ...	20·0	54·67	31·07	25·27	13·01
SbPh₃	14·0	162·61	93·96	31·51	17·70
SbPh₃Cl₂......	20·2	183·94	104·48	33·24	16·18
,, ...	20·0	182·38	103·64	31·61	15·34
,, ...	20·1	179·95	102·04	29·25	13·74
Pb(C₂H₃O₂)₂...	25·2	63·24	36·89	23·04	12·89
PbEt₄	22·4	99·75	58·51	33·75	17·87
SnCl₂	26·2	49·58	27·74	29·98	15·70
SnMe₄........	25·5	71·32	41·73	35·72	19·33
SnEt₄........	19·1	92·36	54·76	26·36	14·12

The refraction constants of mercurydiphenyl were determined in an 8·6 per cent. benzene solution, and those of mercurous nitrate in 13·9—21·22 per cent. nitric acid solutions. Antimony trichloride was examined in 13·5 and 22·05 per cent. benzene solutions respectively; triphenylstibene was examined in a 19·7 per cent. benzene solution, and its dichloride in 18·4, 20·6, and 22·5 per cent. benzene solutions respectively. The constants of lead acetate and stannous chloride were determined in 38·5 and 63·9 per cent. aqueous solutions respectively. All the other substances were examined in the pure liquid state; the molecular weights of the organo-metallic compounds were found to be normal by cryoscopic determinations in benzene solution. Many of the molecular refractions determined by the author differ considerably from those given by Gladstone (*Phil. Trans.*, 1870, i, 9).   W. J. P.

Constitution of Combined Water in Organic Salts. By B. KOSMANN

(*Ber.*, **27**, 1911—1912).—A reply to Surawicz (this vol., ii, 346), in which the author claims to have published similar conclusions in the year 1889, these being deduced from the "theory of hydration" proposed by him.   H. G. C.

Constitution of Complex Metallammonium Bases. By N. KURNAKOFF

(*J. Russ. Chem. Soc.*, **25**, 693—746).—In this paper the author collates and discusses in detail the various constitutions which have been attributed to the complex metallammonium bases. He is of opinion that the most reasonable formulæ for the salts are of types such as $M—a—Cl$, $M{<}^a_a{>}Cl$, $M{<}^a_a{<}^a_a{>}Cl$, &c., where M is an atom of the metal, and a a molecule of ammonia, or of a similar compound.   J. W.

Dimorphism of Potassium Fluoroborate. By C. MONTEMARTINI

(*Gazzetta*, **24**, i, 478—480).—On adding to hydrofluoric acid, boric acid and then potassium carbonate, a gelatinous precipitate falls; this, when dried at 100°, is converted into very minute crystals of potassium fluoroborate belonging to the cubic system and showing the octahedron and dodecahedron.

The small, lustrous crystals, obtained by spontaneous evaporation of an aqueous solution of the salt, belong to the orthorhombic system, $a : b : c = 2·7898 : 1 : 1·2830$.   W. J. P.

Action of Potassium Cyanide on Gold and on some other Metals and Minerals. By G. A. GOYDER

(*Chem. News*, **69**, 262—263, 268—270, 280—281).—Minerals, not in a state of purity, but sufficiently freed from associated minerals to render any action of the latter insignificant, were crushed and sifted through a sieve with 30 holes to the linear inch; 10 parts of each crushed mineral was then placed in a stoppered bottle with 100 parts of a solution containing 1 per cent. of 91·5 per cent. potassium cyanide. The bottles were protected from light, shaken vigorously six times at intervals of an hour, and, after standing all night, the clear, supernatant liquid was examined for copper,

and for free potassium cyanide, with the following results expressed in grains per gallon.

Mineral.	Copper dissolved.	Potassium cyanide remaining in solution.
Azurite	142·7	100·0
Malachite	148·4	6·5
Native copper	159·6	122·6
Copper glance	43·6	0·0
Copper pyrites........	33·6	364·0
Iron pyrites	4·5	628·5
Quartz	—	656·2

Argentite was also dissolved, but iron and zinc sulphides were not. Cyanide solutions saturated with copper minerals did not dissolve gold. Lead, bismuth, antimony, arsenic, tin, cadmium, and mercury were exposed in a 6 per cent. solution of potassium cyanide, and were observed to dissolve with the absorption of oxygen, the action in some cases being very slow ; magnesium, zinc, aluminium and copper, and cobalt, nickel, and iron reduced by hydrogen or carbonic oxide, under similar circumstances, dissolved with evolution of hydrogen, the quantity, in the case of copper, approximating to the change expressed by the equation $Cu_2 + 4KCy + 2H_2O = Cu_2Cy_2 + 2KCy + 2KHO + H_2$. But neither iron nor steel wire acted on potassium cyanide or aurocyanide. Other experiments confirmed the views generally entertained : (1) that the presence of oxygen is required to effect the solution of gold, &c., in solutions of potassium cyanide ; (2) that under the influence of an electric current such solutions deposit their metallic contents, whilst the potassium cyanide gradually undergoes decomposition into potassium and ammonium carbonates, and that if the current is interrupted, the gold redissolves as long as sufficient potassium cyanide remains in solution.

<div align="right">D. A. L.</div>

Action of Sodium Peroxide on Iodine and on Lead Oxide.

By M. HOEHNEL (*Arch. Pharm.*, **232**, 222—225).—When iodine (4 parts) is mixed with sodium peroxide (10 parts) and the mixture is locally heated, an action begins and spreads throughout the mass, a mixture of sodium hydrogen periodate, $Na_2H_3IO_6$, sodium iodide, and iodate being formed. The same products are obtained when sodium iodide is heated with sodium peroxide.

When lead oxide is mixed with water, and sodium peroxide added until the mass becomes white, sodium metaplumbate, $Na_2PbO_3 + 4H_2O$, is formed. It may be washed with 50 per cent. alcohol, and dried over oil of vitriol ; it is white and crystalline ; water decomposes it, yielding at first a yellow acid salt, $NaHPO_3 + 3H_2O$, but ultimately lead peroxide, which is also separated on treating the product with dilute acids. The author has obtained good results by using sodium peroxide for oxidising iron pyrites, but all crucibles are attacked during the process ; a platinum crucible may lose 0·05—0·1 gram at each operation.

<div align="right">A. G. B.</div>

Solubility of Silver Chloride, Bromide, and Iodide in Inorganic and Organic Solvents. By E. VALENTA (*Monatsh.*, **15**, 249—253).—The following table gives the results obtained by the author.

Solvent.	Concentration.	100 grams of solution contain in grams.		
		AgCl.	AgBr.	AgI.
Na₂S₂O₃	1 : 100	0·40	0·35	0·03
	5 : 100	2·00	1·90	0·15
	10 : 100	4·10	3·50	0·30
	15 : 100	5·50	4·20	0·40
	20 : 100	6·10	5·80	0·60
(NH₄)₂S₂O₃	1 : 100	0·57		
	5 : 100	1·32		
	10 : 100	3·92		
Na₂SO₃	10 : 100	0·44	0·04	0·01
	20 : 100	0·95	0·08	0·02
(NH₄)₂SO₃	10 : 100	trace	trace	trace
(NH₄)₂CO₃	10 : 100	0·05		
NH₃	3 : 100	1·40		
	15 : 100	7·58		
MgCl₂	50 : 100	0·50		
KCN...................	5 : 100	2·75	6·55	8·23
NH₄SCN	5 : 100	0·08	0·21	0·02
	10 : 100	0·54	2·04	0·08
	15 : 100	2·88	5·30	0·13
KSCN	10 : 100	0·11	0·73	
Ca(SCN)₂...............	10 : 100	0·15	0·53	0·03
Ba(SCN)₂...............	10 : 100	0·20	0·35	0·02
Al₂(SCN)₆	10 : 100	2·02	4·50	0·02
Thiocarbamide	10 : 100	0·83	1·87	0·79
Allylthiocarbamide......	1 : 100	0·40	0·08	0·008
	5 : 100	1·90	0·35	0·05
	10 : 100	3·90	0·72	0·09

The author discusses the bearing of the above results on the practice of photography.   E. C. R.

Hydrobromide of Cupric Bromide and a Red Cupric Potassium Bromide. By P. SABATIER (*Compt. rend.*, **118**, 1260—1263). —If a brown aqueous solution of cupric bromide is mixed with a concentrated solution of potassium, or calcium, or lithium bromide, a purple solution is obtained with a colour and absorption spectrum similar to those of solutions of cupric bromide in hydrobromic acid (this vol., ii, 352). The colour disappears in dilute solutions. The view that the purple colour is due to the formation of anhydrous cupric bromide consequent on a dehydrating action of the hydrobromic acid or alkali bromide is untenable, because the colour is obtained with hydrobromic acid of the composition HBr,5H₂O, and even with acid of the composition HBr,12H₂O or

$HBr,13H_2O$. Moreover, the solutions in the concentrated acid lose their colour at 100°, but regain it on cooling. The solutions of the anhydrous bromide in absolute alcohol have an absorption spectrum which is independent of the proportion of bromide, and since the green hydrated bromide is efflorescent, it is unlikely that it would exist in presence of anhydrous alcohol; and, moreover, the alcoholic solutions when heated become more opaque, without any change of colour. The purple mixtures of cupric and sodium bromides when concentrated yield green crystals of the hydrate, $CuBr_2.4H_2O$. It would seem probable, therefore, that the red-brown solutions really contain the anhydrous salt, whilst the purple solutions contain a hydrobromide or a double bromide.

When gaseous hydrogen bromide is passed into a concentrated aqueous solution of cupric bromide, black crystals of the anhydrous bromide separate, but their solubility seems afterwards to increase, and if the purple fuming liquid is cooled, it deposits black, lustrous crystals which readily decompose with evolution of hydrogen bromide, and which most probably have the composition $CuBr_2,HBr,2H_2O$, although the results of analysis agree more closely with the formula $3CuBr_2,2HBr,6H_2O$.

When the mixed solutions of bromides are concentrated, they yield, as a rule, only crystals of the green hydrated cupric bromide, but the author has succeeded in isolating an anhydrous cupric potassium bromide, $CuBr_2,KBr$, in deliquescent, rhombic lamellæ, which are very opaque and almost black, but are red in very thin layers. The crystals seem to be monoclinic with the faces p, h', g', the angle $p : h'$ being about 65°. When heated, the crystals give off one-third of their bromine, and melt to a black, very limpid liquid which solidifies to a greyish glass. The latter, when treated with water, yields potassium bromide and insoluble cuprous bromide. C. H. B.

Stability of Aqueous Solutions of Mercuric Chloride. By E. BUERCKER (*Compt. rend.*, 118, 1345—1347).—The author has made observations similar to those of Vignon and Tanret (this vol., ii, 93) on the stability of aqueous solutions of mercuric chloride containing 1 part of the salt per 1000. He finds that ordinary spring water causes immediate decomposition of the mercuric chloride, and this decomposition continues under the combined influence of air and light, and the inorganic and organic substances contained in the water and in the air. Decomposition stops or becomes insignificant when the liquid is removed from the action of air and light. Solutions of mercuric chloride, prepared by means of pure distilled water, alter to only a very minute extent, even when exposed to air and light. C. H. B.

Ternary Alloys containing Aluminium. By C. R. A. WRIGHT (*Proc. Roy. Soc.*, 55, 130—139; compare Abstr., 1893, ii, 522).—Cadmium is but slightly soluble in aluminium, and aluminium practically not at all in cadmium. Tin, however, acts as a solvent to both metals, and an examination of the ternary alloys that it forms with them shows that the aluminium-cadmium-tin critical curve is

depressed as regards the aluminium-lead-tin one. and probably also as regards the aluminium-bismuth-tin curve. Alloys of aluminium and lead (or bismuth), with antimony as solvent, show an excrescence in the central part of the critical curve, due to the separation of the difficultly fusible compound SbAl. The same reason causes an excresence in the aluminium-lead-antimony curve, which is raised with respect to the zinc-lead-antimony curve, depressed as regards the aluminium-lead-tin one. An excresence again appears, and for the same reason, in the aluminium-bismuth-antimony curve, which is depressed relatively to the aluminium-lead-antimony curve, and, like the zinc-bismuth-antimony curve, exhibits an inward depression at the point aluminium 65·22, bismuth 25·52, antimony 9·26 per cent., the ratio of bismuth to antimony corresponding with the alloy, Sb_2Bi_3.   C. F. B.

Analysis of an Ancient Slag. By W. THOMASON (*Chem. News*, **69**, 303).—The following are the numbers obtained from the analysis of a sample of slag, from the heaps long known as "Dud Dudley's slag," from the Netherton district of Staffordshire.

FeO.	Fe_2O_3.	MnO.	Al_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	SiO_2.
41·90	7·92	0·20	15·82	2·24	1·73	1·15	0·72	28·15

Total.	Sulphur and	Phosphorus.
99·83	0·024	0·424 per cent.

The sample was vitreous with numerous blow-holes, and was evidently a product of an old direct process when the siliceous matter and gangue were slagged off as iron silicate without the addition of lime.   D. A. L.

Molecular Changes of Carbon and Iron accompanying the Tempering of Steel. By G. CHARPY (*Compt. rend.*, **118**, 1258—1260).—The author has compared the condition of the carbon as determined by Eggertz's method with the condition of the iron as indicated by the rectilinear break in the curve of extension under longitudinal strain. The proportion of carbon determined in this way is lower the harder the temper of the steel. Experiments were made with a number of bars from the same ingot of Siemens-Martin steel containing 0·71 per cent. of carbon. These bars were tempered by different methods, and their physical properties and the proportion of carbon (by Eggertz's method) were determined. When the bars were heated below 750° there was no change in the condition of the carbon, but in some cases there was partial modification of the iron, although no relation could be traced between this modification and the breaking charge. The increased resistance of the steel is probably due to change in its mechanical structure as shown by the fracture.

When the steel was tempered after heating above 740°, the iron and carbon showed simultaneous modification, the iron being completely transformed in all the bars that showed a breaking strain higher than 82 kilos. The proportion of carbon transformed diminished continuously as the breaking strain rose and the elongation

diminished. Bars with a breaking strain lower than 90 kilos. were readily attacked by files and other tools, and were not tempered in the proper sense of the word. Hard temper is accompanied by a high breaking strain and a reduction in the proportion of carbon as determined by Eggertz's method. C. H. B.

Potassium Chlorochromate. By G. HERFELDT (*J. pr. Chem.*, [2], **50**, 93—94).—This salt is best prepared by dissolving 3 parts of potassium dichromate in 4 parts of concentrated hydrochloric acid by the aid of a gentle heat. Contrary to the statement of Heinze, the salt does not lose chlorine at 100°; this does not occur below 250°, and even after some hours' heating at 500—600° about 8 per cent. of the chlorine remains in the residue. The action of the salt on organic compounds is an oxidising one. An attempt to prepare chlorochromic anhydride by the action of chromyl chloride on chromic anhydride is described. A. G. B.

Alkali Aurochlorides and the separation of the Alkalis. By R. FASBENDER (*Chem. Centr.*, 1894, i, 409—410 ; from *Nederl. Tijdschr. Pharm.*, **6**, 1—4).—Sodium aurochloride, $NaCl, AuCl_3 + 2H_2O$, is soluble in water, alcohol, and ether, and crystallises from all these solvents with the same amount of water of crystallisation. The potassium salt is not soluble in ether, and crystallises from alcohol without water of crystallisation. The lithium salt, when purified by washing with ether, contains $4H_2O$, and is not as stable as the sodium or potassium salts. The difference in solubility of these salts may be employed to separate sodium and potassium chlorides. Excess of gold chloride should be avoided, and the double salts must be dried at 100—110° to drive off all traces of acid, as these tend to make the potassium salt soluble in ether. These salts can also be employed for separating lithium and probably rubidium from sodium and potassium. L. T. T.

Mineralogical Chemistry.

Composition of Apophyllite. By C. FRIEDEL (*Compt. rend.*, **118**, 1232--1237).— Gentil found that apophyllite from Bou Serdoun, near Collo, Algeria, contained no fluorine, and the author confirms this statement. He also finds that this apophyllite, and five other specimens from widely different localities, when heated to redness give off water which has an alkaline, and not an acid, reaction. They contain small quantities of ammonia, part only of which is given off on heating to redness, and the remainder can be liberated by boiling with soda solution. Pisani has found that nine specimens of the mineral from different localities give off water which is neutral to test paper, whilst only one specimen from Feroe gave off water with an acid reaction.

Direct examination of several specimens for fluorine gave negative results, and the author concludes that, contrary to usual statements which seem to be based only on indirect evidence, this element is not an essential constituent of apophyllite.　　　　　　　　　C. H. B.

New Variety of Meteorite. By G. HINRICHS (*Compt. rend.*, **118**, 1418--1420).--The crust of meteorites is usually black, whilst the mass of the stone is greenish, the black crust having been produced by the action of heat, and its thickness indicating the depth to which this action has penetrated. A specimen which recently came into the author's possession has, on the contrary, a white crust whilst the mass of the stone is almost black. The crust consists of calcium sulphide, CaS. It can readily be produced artificially by holding a black fragment of the meteorite perpendicularly in a blowpipe flame just beyond the hottest point.

The mass of the meteorite has a mean composition agreeing closely with the pyroxene-tadjerite described by Meunier. Its sp. gr is 3·44. It contains 8 per cent. of meteoric iron, two-thirds of which is in somewhat large grains, troilite in quantity almost as large as that of the iron, and pyroxene and peridote, the latter being present in larger proportion than the former.　　　　　　　　　C. H. B.

Analysis of the Meteoric Stone from Makariwa, near Invercargill, New Zealand. By L. FLETCHER (*Proc. Roy. Soc.*, **55**, 142—145).—The meteorite, before weathering, contains nickel-iron, 5·20; olivine, 49·08; enstatite, 38·77; troilite, 6 00; schreibersite, 0·64, chromite, 0·31 per cent. Interest centres chiefly in the method of analysis, which is to be described in full in the *Mineralogical Magazine.* A separation is first made by means of a magnet; but as the metal present is partly oxidised, it is necessary to extract the unattracted part with mercuric ammonium chloride (after estimating the sulphur and phosphorus in it), heat the residue to a dull red heat in a current of hydrogen, and again extract; metal and metallic oxide are thus removed. The silicate portion is only slightly affected by this treatment, but the troilite and schreibersite are largely affected, and it is necessary (by estimating the sulphur and phosphorus in the residue after extraction) to allow for iron and nickel that have passed into solution from these minerals. The residue is then extracted three times with hydrochloric acid (sp. gr. 1·06) on the water bath; this completely destroys the olivine, the silica of which is then removed by extraction with aqueous sodium carbonate containing a little soda. The residual undecomposed silicate, enstatite, is separately analysed. Various determinations of the alkalis were also made.　　　C. F. B.

Analysis of Water from the Hot Springs of Monte Irone, Abano. By R. NASINI and F. ANDERLINI (*Gazzetta*, **24**, i, 327—342). —A number of springs of hot water are found at Monte Irone; the temperature of the water is not the same at all the sources, but the maximum temperature was 87° on a cold January day. The water issues accompanied by gas which contains 75 per cent. of nitrogen,

11 of carbonic anhydride, 8—12 of methane and other hydrocarbons, and 1·7—2 per cent. of hydrogen sulphide. The water is slightly alkaline, and at 20°/4° has the density 1·0026. The quantities of the various dissolved substances are given in the following table in parts per 10,000 by weight.

Substance.	Parts per 10,000.	Substance.	Parts per 10,000.
NaCl	34·0294	KCl	1·5332
NH$_4$Cl	0·1165	LiCl	0·0128
MgCl$_2$	3·0674	MgBr$_2$	0·0973
MgI$_2$	0·0040	NaHCO$_3$	1·4824
CaH$_2$(CO$_3$)$_2$	0·8970	FeH$_2$(CO$_3$)$_2$	0·0116
CaSO$_4$	12·6310	Al$_2$O$_3$.	0·0015
SiO$_2$	0 6639		

Total solid residue dried at 180° = 53·4850.

Traces of organic matter, boric acid, strontium, manganese, arsenic, and phosphoric acid are also present. W. J. P.

Physiological Chemistry.

Respiration Apparatus, by F. HOPPE-SEYLER (*Zeit. physiol. Chem.*, **19**, 574—589); **Respiration in Man,** by E. LAVES (*ibid.*, 590—602); **Respiration in Cases of Diabetes Mellitus,** by W. WEINTRAUD and E. LAVES (*ibid.*, 603—628); **Respiration in a Dog after Extirpation of the Pancreas,** by the same (*ibid.*, 629—646).—The apparatus used in the investigations above quoted is one adapted for human beings on the principle of Regnault's well-known one. Its construction is illustrated by figures. In a normal individual, the average figures obtained from seven experiments, each of which is given fully, are the following.

Oxygen used, per diem	400·7 litres
,, per kilo. per minute	4·107 c.c.
Carbonic anhydride produced per diem	324·5 litres.
,, ,, ,, per kilo. per minute	3·52 c.c.
Respiratory quotient....................	0·857

The results obtained in a diabetic patient show that the amount of oxygen consumed is about the same as in a healthy individual; the respiratory quotient is a little lower. The administration of carbo-hydrate food, selected so as to cause no corresponding output of sugar in the urine, causes an increase in the production of carbonic

anhydride and a rise of the respiratory quotient as in the case of healthy individuals.

In the dog, no noteworthy differences in the respiratory exchange were observable after extirpation of the pancreas.   W. D. H.

Estimation of the Acidity of the Stomach. By P. MOHR (*Zeit. physiol. Chem.*, **19**, 647—650).— A few experiments are recorded in which G. Töpfer's method of estimating the acidity of the contents of the stomach (this vol., ii, 262) was used. They show that the method is trustworthy.   W. D. H.

Lymphagogues. By E. H. STARLING (*J. Physiol.*, **17**, 30—47).— The formation of lymph is considered by Heidenhain to be due to a process of secretion by the endothelial cells of the vascular wall; and lymphagogues are substances which cause an increased flow of lymph. These may be divided into two classes; the first class includes substances like peptone and leech extract, which cause an increased flow of more concentrated lymph; the blood plasma is diminished both in quantity and concentration. The second class includes sugar, salt, and other crystalloïds; they cause an increased flow of more watery lymph; the blood at the same time becomes more watery also, so that the excess of lymph is derived from the tissues.

An examination of the experiments on which these views rest has led the author (*J. Physiol.*, **16**, 224) to hold that lymph formation is not a vital secretory process, but that it can be explained by mechanical factors, difference of blood pressure, &c.; and the present paper is devoted to a fuller exposition of this view with fresh experiments in which lymphagogues of both classes were used. It is held that the differences in lymph flow can all be explained as due to differences in intracapillary pressure and permeability of the vessel walls. An important point strongly insisted on, is that arterial pressure is no measure of intracapillary pressure, but must be considered in relation to the pressures in the outlet from the capillary area, that is, in the veins.

Members of the second class of lymphagogues on injection into the blood attract water from the tissues and cause a condition of hydræmic plethora with increased capillary pressure. The increased lymph flow from the thoracic duct is due to the increased pressure in the abdominal capillaries.

Members of the first class of lymphagogues are really poisons which affect injuriously (1) the endothelial cells of the capillaries, especially in the liver, increasing their permeability; (2) the muscular walls of the blood vessels, especially in the splanchnic area, producing vascular dilatation; and (3) the heart muscle. The increased lymph flow is almost entirely due to the increased permeability of the hepatic capillaries.   W. D. H.

Physiological and Therapeutic Effects of the Homologues of Quinine. By E. GRIMAUX, LABORDE, and BOURRU (*Compt. rend.*, **118**,

1303—1306).—The authors have investigated the toxic and thera-
peutic effects of cupreine, $C_{19}H_{21}N_2O\cdot OH$, quinine (methylcupreine),
$C_{19}H_{21}N_2O\cdot OMe$, and their higher homologues up to and including
amylcupreine. Both toxic and therapeutic effects increase with
the molecular weight. Ethylcupreine is a more powerful febrifuge
than quinine, and propylcupreine may be useful in cases of high
fever, but its toxic action is so powerful that it can only be adminis-
tered in small doses.   C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Fluorine Compounds on Beer Yeast. By J. EFFRONT (*Compt. rend.*, **118**, 1420—1423).—The author has compared the chemical effects of ordinary yeasts and of yeasts inured to the action of fluorine compounds (this vol., ii, 62). For a given quantity of alcohol formed, the quantity of carbonic anhydride liberated is always distinctly higher with the ordinary yeast. For a given quantity of glucose decomposed, the quantity of alcohol formed is distinctly higher, and the quantity of glycerol and succinic acid lower, with the yeast inured to fluorine compounds than it is when ordinary yeast is employed. C. H. B.

Constituents of the Tissues of Fungi. By E. WINTERSTEIN (*Zeit. physiol. Chem.*, **19**, 521—562).—In this research, numerous members of the fungus group were investigated by methods similar to those employed by E. Schulze. The chief constituent is undoubtedly a substance which resembles cellulose, and in some of its properties the true cellulose of Schulze (this vol., ii, 250); hemicellulose appears to be present, and can be extracted by means of hot, dilute acids The fungus-cellulose ("Pilzcellulose") of de Bary is a mixture of cellulose with some nitrogenous substance, which, however, is not proteïd in nature. Full references are given to previous work on the subject. W. D. H.

Alkaline Reaction during Assimilation in Aquatic Plants. By O. LOEW (*Chem. Centr.*, **65**, i, 510; from *Flora*, **77**, 419).—According to Hassack, the alkalinity produced by various aquatic plants is due to the hydrogen calcium carbonate in the nutritive solutions, and the production of normal carbonate, due to a separation of alkali by the plant. The author, however, in the case of elodea, observed that not only solutions containing calcium hydrogen carbonate became alkaline, but also those containing calcium nitrate. This was not due to ammonium carbonate, as no ammonia was present. Elodea also gradually reddened a solution of phenolphthalein in distilled water, and in eight hours calcium could be detected in the solution; organic matter was also detected. It is concluded that the reddening of

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phenolphthalein is caused either by some organic calcium compound, or that calcium carbonate is held in solution in a colloïdal state by the separated organic matter, and that this has the power of reddening phenolphthaleïn. A similar result was, in fact, obtained by shaking a warmed solution of calcium hydrogen carbonate with some gum arabic and phenolphthaleïn in a capacious flask until the loosely combined carbonic anhydride had separated.　　　　N. H. M.

Oats Manured with Ammonium Sulphate. By C. MITRAKEV (*Chem. Centr.*, **65**, i, 560; from *Inaug. Diss.*, Leipzig, 1892).—Exclusive nitrogenous manuring increased the proteïds and lowered the quantity of fat and non-nitrogenous extract of the grain. The varieties of oats which gave the greatest yield had larger grains, but were poorer in proteïds than the other varieties. Heavy grains are richer in proteïds than light grains. The small grains produced on rich soil are richer in proteïds than the larger grains, whilst in the case of poor soil the reverse holds good. Increase in amount of proteïd goes with decrease of fat and non-nitrogenous extract.

　　　　　　　　　　　　　　　　　N. H. M.

Analytical Chemistry.

Electrolytic Estimation of the Halogens. By G. VORTMANN (*Monatsh.*, **15**, 280—284).—A dense reguline deposit of silver haloïd is obtained when a halogen is deposited on a weighed silver plate from an alkaline solution. The solution of the halogen is mixed with a few grams of alkali tartrate and 10 per cent. sodium hydroxide solution, and subjected to a current of 2 volts and 0·03—0·07 ampère. A platinum cathode is employed, and an anode of pure silver. The end of the electrolysis is determined when a new anode placed in the solution does not gain in weight. The anode after being removed from the solution, is washed with water, and then with alcohol, and dried over a Bunsen burner; finally it is heated until the silver haloïd darkens or melts, and is then allowed to cool, and weighed. If a very accurate estimation is required, it is necessary at the end of the operation to substitute a platinum electrode for the silver anode, and again pass the current for one hour, in order to deposit the small quantity of silver which is dissolved.

The results obtained by the author with potassium iodide are satisfactory. The iodine in a solution as iodate may also be determined by this method. E. C. R.

Detection of Traces of Chlorine. By A. VILLIERS and M. FAYOLLE (*Compt. rend.*, **118**, 1413—1414).—The sensitiveness of the reaction previously described (this vol., ii, 396) varies considerably with different specimens of aniline, and is highest when the aniline contains small quantities of toluidine. By using orthotoluidine in

place of aniline (*loc. cit.*), an intense blue coloration is obtained, becoming violet-red on heating or after some time. The reaction is very distinct with as little as 0·1 milligram of chlorine.

When bromine is present, if orthotoluidine is used alone, it has the disadvantage that the precipitate produced by the bromine does not remain perfectly white. This difficulty is removed by employing as the reagent a mixture of a saturated aqueous solution of aniline (100 c.c.), saturated aqueous solution of orthotoluidine (20 c.c.), and glacial acetic acid (30 c.c.). So long as the reagent is in excess, no bromotoluidine is formed, but the bromine is converted into the stable and perfectly white bromaniline.

The action of chlorine on orthotoluidine in acid solution seems to be a rapid and easy method of preparing safranines.

Chlorine water may be used as a test for the presence of toluidine in aniline; if the latter is pure, the coloration will be brownish, but if the former is present in not too small quantity, the coloration will be first blue and then violet. C. H. B.

Estimation of Chlorides in Products of Organic Origin. By G. MEILLÈRE (*J. Pharm.*, [5], **29**, 497—499).—When chlorine has to be estimated in organic products, it is necessary to burn off the organic matter, but this always causes an appreciable loss of chlorine.

The author recommends the following process. The substance (urine, for instance) is mixed with an equal bulk of 20 per cent. solution of calcium nitrate and evaporated to dryness in a flat-bottomed platinum dish; a slight elevation of temperature suffices to completely burn off the carbonaceous matter. The residue when treated with water yields a filtrate which is free from phosphates; to this a drop of solution of tropæolin is added, and then dilute sulphuric acid to acid reaction. A little powdered chalk is now added to decolorise the liquid, and the chlorine is titrated with silver nitrate, using potassium chromate as indicator. It is advisable to make a blank experiment. L. DE K.

Separation of Chlorine from Bromine. By R. ENGEL (*Compt. rend.*, **118**, 1263—1265).—1 to 2 grams of the substance is dissolved in 150—200 c.c. of water, mixed with 3 to 5 grams of ammonium persulphate, and heated at 70—80°. A current of air is passed into the liquid for about an hour in order to remove the bromine, which is best collected in a solution of sulphurous acid and estimated as silver bromide. It is not advisable to collect the bromine in potassium iodide solution, since small quantities of ozone, or possibly of persulphuric anhydride, may be given off. Under the conditions specified, the quantity of chlorine liberated from solutions of chlorides is very minute, and probably does not exceed 0·1 milligram.

Iodine can also be separated by means of ammonium persulphate, the cold liquid being mixed with sodium acetate and the persulphate, and the iodine removed by means of carbon bisulphide. Under these conditions, no trace of bromine or chlorine is liberated.

C. H. B.

Detection of Hydrobromic acid. By A. VILLIERS and M. FAYOLLE (*Compt. rend.*, **118**, 1265—1268).—The well-known method of detecting bromides in presence of iodides, by liberating the two halogens successively by gradual addition of chlorine water, gives unsatisfactory results, owing partly to the fact that some bromine is liberated while iodides still remain undecomposed, and partly to the formation of iodine bromide. The brown coloration following the violet cannot be distinctly recognised when the quantity of bromine present is less than one-tenth of the quantity of iodine. In complete absence of iodine, however, a very distinct yellow coloration is imparted to carbon bisulphide by 1 milligram of bromine.

In order to remove iodine, the liquid, which should be free from nitric acid, is mixed with an excess of ferric chloride solution containing no free chlorine. About 5 c.c. of a half-normal solution should be added for every 0·1 gram of iodine supposed to be present. The liquid is evaporated to dryness on a water bath, and heated for an hour or two, in order to ensure complete volatilisation of the iodine. The residue is dissolved in a small quantity of water, the iron precipitated by means of an alkali, and the filtrate acidified with hydrochloric acid and treated with chlorine water and carbon bisulphide.

In the ordinary course of an analysis, it would be best to operate on the precipitate of silver haloïd salts, hydrocyanic acid having been previously removed (this vol., ii, 396). The silver precipitate is heated with hydrogen sulphide, and the liquid concentrated after removal of the excess of the gas.

In order to detect bromine in iodine, the halogens must first be converted into the hydracids by treatment with hydrogen sulphide in presence of water.　　　　　　　　　　　　　　　　　C. H. B.

Estimation of Iodine. By A. VILLIERS and M. FAYOLLE (*Compt. rend.*, **118**, 1332—1335).—The solution, which must be free from nitric acid, is mixed with ferric chloride solution containing no free chlorine (5 c.c. of a half-normal solution for every 0·1 gram of iodine), and agitated with carbon bisulphide. The latter is then drawn off, and a fresh quantity is added and agitated with the liquid, the process being repeated until the carbon bisulphide remains colourless. As a rule, four washings suffice. The several quantities of the bisulphide are mixed, washed with a little water to remove any traces of ferric chloride, and the iodine estimated with sodium thiosulphate solution.

A convenient form of apparatus for extracting with carbon bisulphide and washing the latter, consists of two cylindrical bulbs separated by a stop-cock. The upper end of one bulb is fitted with a glass stopper, and the lower end of the other is provided with a second stop-cock.

The chlorine, bromine, and iodine may be precipitated as silver salts, which are then decomposed by means of hydrogen sulphide and the excess of the latter expelled, the filtrate being treated in the manner described.　　　　　　　　　　　　　　　　　C. H. B.

Detection of Iodine in Urine. By H. SANDLUND (*Arch. Pharm.*, **232**, 177—183).—Of the methods recommended for the detection of iodine in urine (see Neubauer and Vogel, "*Harnanalyse*") the author finds the following to be the most delicate and trustworthy : To 5 c.c. of the urine there are added successively 1 c.c. of sulphuric acid (1 : 4), 1—3 drops of dilute sodium nitrite solution (1 : 500), and carbon bisulphide or chloroform ; after agitation, the solvent will be coloured rose-red by a smaller proportion of iodine than 0·001 per cent. ; indeed, if a comparison with a tube containing urine known to be free from iodine be made, as little as 0·00000765 gram of iodine in 5 c.c. of urine can be detected by this test.

The two methods which the author has devised for the quantitative estimation of iodine in urine are as follows, the second being recommended for very small quantities of iodine, on account of the fact that filtration is avoided : 1.— 25—50 c.c. of the filtered urine is acidified with nitric acid, and sufficient silver nitrate is added to precipitate all the iodine; after half-an-hour's digestion, the precipitate is collected, washed, and transferred, with the paper, to a flask, in which it is heated with water (8 c.c.), hydrochloric acid of sp. gr. 1·124 (4 c.c.), and zinc dust (2 grams). When reduction is complete, the contents of the flask are filtered into a distillation flask, and the filtrate is distilled with ferric chloride (3—4 grams), the distillate being received in a solution of potassium iodide, and the iodine titrated with a solution of sodium thiosulphate (N/50 or N/100) in the usual way. 2.— 25—50 c.c. of urine (or more if the iodine content be very low) is evaporated to dryness in a platinum dish with sodium carbonate (0·25—0·5 gram) ; the residue is ignited to burn off organic matter. dissolved in water, and the solution, after being acidified with hydrochloric acid, is distilled with ferric chloride ; the iodine is then determined in the manner described above.　　　　A. G. B.

Estimation of Nitric acid. By BARILLÉ (*J. Pharm.*, [5], **29**, 441—444).—The author, remarking on an article by Henry (this vol., i, 252), states that, as long ago as 1878, he had proposed the use of the nitrometer for the estimation of nitrates in potable waters.
　　　　　　　　　　　　　　　　　　　　　　　L. DE K.

Application of Sodium Peroxide in Analysis. By O. KASSNER (*Arch. Pharm.*, **232**, 226—240).—The author has detected ozone in the oxygen which is evolved when sodium peroxide is dissolved in water, and attributes the activity of sodium peroxide as an oxidising agent to its presence. When sodium peroxide is added to a solution of uranyl nitrate, the yellow precipitate, which is at first formed, redissolves, and from the solution Fairley's sodium peruranate may be precipitated by alcohol. Whilst chromium hydroxide readily passes into solution as sodium chromate (Haussermann, Abstr., 1893, ii, 471), manganous hydroxide is only oxidised to the hydrated peroxide, and ferrous hydroxide to ferric hydroxide. Upon these facts, the author bases a process for separating chromium from manganese and iron which is obvious (compare Clark, Trans., 1893, 1079). If sodium peroxide is substituted for a mixture of sodium carbonate and potassium nitrate as an oxidant for manganese oxides, an excess must

be avoided, otherwise, on dissolving the product in water, the manganate will be reduced by this excess. Sodium peroxide may be substituted for hydrogen dioxide in the method described by G. Kassner (Abstr., 1891, 245), which may be applied for the estimation of potassium ferricyanide. Cobalt is precipitated as black sesquioxide by sodium peroxide, but nickel remains as the green hydroxide; neither metal is precipitated by this reagent from a potassium cyanide solution. Mercury, gold, and silver salts are reduced to the corresponding metals by sodium peroxide; but the solutions of chloroplatinic and chloropalladious acids are not reduced, since their sodium salts appear to be stable; solutions of platinic and palladious chloride, obtained by adding silver nitrate to the acids, are, however, reduced.

For the quantitative separation of antimony, tin, and arsenic, sodium peroxide may be applied as follows. The mixed sulphides are stirred with about 30 c.c. of water, and sodium peroxide is added by degrees, until a small portion no longer gives a coloured precipitate on the addition of dilute sulphuric acid. The whole is then transferred to a silver crucible, evaporated to dryness, and kept in fusion for some time. The melt is treated with aqueous alcohol (3 : 1), and the undissolved sodium pyroantimonate collected on a filter and weighed as antimonyl antimonate. After the alcohol has been evaporated from the filtrate, this is acidified with dilute sulphuric acid, the precipitated stannic acid is dissolved by caustic soda, and carbonic anhydride is passed through the solution to incipient precipitation; ammonium chloride is then added, and the solution heated for half an hour to completely precipitate the stannic oxide, which is weighed as usual. The arsenic is precipitated from the second filtrate by magnesia mixture.

Qualitatively, the method may be modified by testing a small portion of the oxidised mixture (care having been taken that all the sodium peroxide has been previously decomposed by boiling) for antimony by adding a little of the liquid to some acidified potassium iodide solution; if antimony be present, it will be separated on adding alcohol after a somewhat prolonged digestion with sodium peroxide.

A. G. B.

Separation of the Alkalis by means of their Aurochlorides. By R. FASBENDER (Chem. Centr., 1894, i, 409—410).—See this vol., ii, 421).

A Test for Copper. By P. SABATIER (Chem. Centr., 1894, i, 657; from Rev. intern. falsif., 7, 101; compare this vol., ii, 352).—If concentrated hydrobromic acid is added to a concentrated solution of cupric bromide, a violet-red hydrobromide is formed, which is but slightly affected by heating the solution, but is decomposed by dilution with water, with production of a blue coloration. If a solution containing a copper salt is added to 1 c.c. of concentrated hydrobromic acid, a purple coloration is produced if much copper is present, a lilac coloration if little. 0·1 milligram copper may be recognised by this test. A mixture of solid potassium bromide and concentrated phosphoric acid may be substituted for the hydrobromic

acid. The mixture should be slightly warmed, the coloration appearing on cooling. L. T. T.

Estimation of Mercury in Presence of Iodine. By FRANÇOIS (*J. Pharm.*, [5], **29**. 493—497).—The author has proved that although mercuric iodide is not completely decomposed by heating with calcium oxide, it is when ignited with soda-lime. The analysis is conducted as usual, in a combustion tube, a little oxalic acid being added to the mixture to yield a current of hydrogen, which will assist in expelling the mercurial vapour. The soda-lime, which should have little tendency to fuse, is best prepared by slaking 4 parts of calcium oxide with 1 part of sodium hydroxide dissolved in 4 parts of water, and igniting the product. If it be desired to estimate the iodine also, the contents of the tube should be transferred to a generating flask, the delivery tube of which dips into a test glass containing a solution of silver nitrate. After first adding some water to slake the lime, nitric acid is *very* gradually added until the mass has dissolved ; the traces of iodine which escape are absorbed by the silver solution. The liquid is then filtered, and the filter, after being moistened with a few drops of sulphurous acid, is well washed. Any free iodine in the filtrate is cautiously reduced by adding a little more sulphurous acid, and the iodine is then precipitated, using the silver nitrate solution from the test-glass. The results obtained by the author are very satisfactory. L. DE K.

Volumetric Estimation of Gold. By G. FRANZESCHI (*Chem. Centr.*, 1894, i, 657 ; from *Bull. Chim. Farmac.*, 1894, No. 2).—Excess of decinormal potassium oxalate is added to the solution containing the gold salt, the whole boiled for a few minutes, and then allowed to cool. The precipitated gold is collected, and the filtrate (to which 1 c.c. of dilute sulphuric acid is added) is warmed and titrated with decinormal potassium permanganate, 1 c.c. of decinormal potassium oxalate destroyed represents 0·0063 gram of gold. The gold solution must not contain free hydrochloric acid. L. T. T.

Separation and Estimation of Small Quantities of Methylic and Ethylic Alcohols. By L PRUNIER (*J. Pharm.*, [5], **29**, 407—410).— After the isolated alcoholic liquid has been treated with concentrated hydriodic acid to convert the alcohols into the corresponding haloid salts, the liquid is shaken with pure chloroform ; or it may be distilled, and the first portions condensed in a receiver containing chloroform. After removing free acid by shaking with aqueous potash, the chloroform is agitated with a solution of silver nitrate and a little moist silver oxide, which, after some time, will cause a precipitate of silver iodide. This is washed, first with ammonia, and then with nitric acid, and weighed. If ethylic alcohol alone be present, its amount may be at once calculated from the weight of the silver iodide ; but if both alcohols are present, their total amount must be ascertained from the specific gravity of the distillate, and their respective amounts calculated from the amount of silver iodide obtained.

The presence of methylic alcohol may be suspected when the chloroformic solution of the hydriodides boils below 61°, also by the alcohol yielding formic acid on oxidation. Ethylic alcohol, on the other hand, may be approximately estimated by determining the amount of iodoform it yields. L. DE K.

Iodometric Estimation of β-Naphthol. By F. W. KÜSTER (*Ber.*, **27**, 1905—1909).—The iodometric method of estimating β-naphthol, described by Messinger and Vortmann (Abstr., 1890, 1473), only gives accurate results when the concentration of the β-naphthol solution is approximately constant, the amount of iodine fixed undergoing considerable variation when this is not the case. In order to determine the amount of β-naphthol in solutions containing from 0·1—0·5 gram per litre, the author made a large number of determinations with known and varying quantities of β-naphthol, using always 100 c.c. of the solution, 0·6 c.c. of 3·6 N soda, and 25 c.c. N/10 iodine; the amounts of thiosulphate required for titrating back were plotted into a curve, from which an iterpolation table was drawn up, showing the amount of β-naphthol corresponding with any volume of thiosulphate solution used, and from this table the amount of β-naphthol in any solution can be determined accurately.

H. G. C.

Testing Phenacetin. By G. GUASTI (*L'Orosi*, **17**, 111—115).— The usual test for the presence of acetanilide in commercial phenacetin consists in heating the suspected sample with soda and alcohol, and then warming with chloroform; if the characteristic odour of the isonitriles is detected, the sample is said to contain acetanilide. The author shows, however, that pure phenacetin gives the isonitrile odour under such circumstances; the test is therefore valueless.

The presence of 4 per cent. of acetanilide in phenacetin may be detected by boiling 0·5 gram of the sample with 10 c.c. of water, cooling, and filtering off the deposited phenacetin; the filtrate is concentrated, boiled with 1 c.c. of concentrated hydrochloric acid, and treated with a little liquid phenol and calcium hydochlorite solution. On adding excess of ammonia, the liquid assumes an indigo-blue colour if acetanilide is present.

The following modification of Hirschsohn's method is sensitive to 0·5 per cent. of acetanilide in phenacetin. 1 gram of the sample is boiled with 15 c.c. of water, and the solution cooled and filtered. If acetanilide is present, the filtrate gives a turbidity with bromine water, due to the deposition of parabromacetanilide. W. J. P.

Estimation of Albumin by Méhu's Process. By L. RUIZAND (*J. Pharm.*, [5], **29**, 364—367).—Méhu recommends coagulating the albumin with phenol and washing the precipitate with a boiling, saturated solution of the same. The author, having tried the method, finds that a very appreciable amount of albumin is dissolved by the washings, but that no appreciable loss is incurred by washing with cold water containing 3—4 per cent. of phenol. L. DE K.

General and Physical Chemistry.

Tautomerism. By J. W. Brühl (*Ber.*, **27**, 2378—2398; and *J. pr. Chem.*, [2], **50**, 119—221. The experimental details are given in the latter paper only).—The author describes substances which contain the group :CH·CO as ketonic, whilst compounds containing the group :C:C(OH) are said to be "enolic." It is difficult, by spectrometric methods, to find whether a ketonic form changes into an enolic form on rise of temperature, inasmuch as neither of the two ordinary expressions for the molecular refraction are quite independent of temperature changes. The molecular dispersion $\left(\dfrac{n^2 - 1}{n^2 + 2} - \dfrac{n_1^2 - 1}{n_1^2 + 2}\right)\dfrac{P}{d}$, is, however, but very slightly affected by changes of temperature, and is therefore of great assistance in such problems. This expression for the dispersion is a highly constitutive one; if its value for a substance at a high temperature is the same as that at a low one, the constitution of the substance is certainly unaffected by the temperature change.

Position isomerides, such as the xylenes, have approximately the same molecular refraction; the differences between the molecular dispersions of aliphatic position isomerides are small, whilst the corresponding differences for aromatic isomerides are somewhat larger. The differences, however, become much greater for derivatives of substances of this class, which contain strongly refractive and strongly dispersive groups.

The results of the present investigation fully confirm the author's previous conclusion, that isomerides containing different kinds of double linkings, such as ethylenic and carbonylic ones, have very different refractive and dispersive powers. The ethylenic bonds have a greater spectrometric constant than carbonylic bonds, whilst the latter, in turn, have a greater optical value than the linkage C·O·C.

Aromatic and aliphatic monoketones, and 1 : 2- and 1 : 4-diketones, behave as true carbonyl compounds. The spectrometric behaviour of the 1 : 3-ketones is however anomalous; the same is true of acetophenone, and, in this case, is due to the proximity of the phenyl- and carbonyl-groups. Acetoformic (pyruvic) acid and acetopropionic (levulinic) acids have the molecular refractions and dispersions of true keto-compounds. This behaviour is quite different from that of acetoacetic acid; the methylic and ethylic salts of the latter, and of its methyl-, ethyl-, dimethyl-, and diethyl-derivatives are analogous in spectrometric behaviour. They are true keto-compounds, and not derivatives of hydroxycrotonic acid as Nef considers; acetoacetates, and mono- and di-alkylacetoacetates therefore have the constitutions COMe·CH₂:COOR, COMe·CHR'·COOR, and COMe·CR'₂·COOR respectively. The spectrometric examination clearly shows that on introducing a carbethoxy-group into the acetoacetates or monalkylacetoacetates, the tautomeric or enolic form of the same type as the hydroxycrotonates is obtained; no reversion to the ketonic form

occurs on heating. A similar change in the acetoacetic nucleus probably occurs on treatment with bases; the so-called ethylic par-amidoacetoacetate is most probably ethylic imidobutyrate, whilst the action of phenylhydrazine on ethylic acetoacetate yields ethylic hydrazocrotonate.

Similarly, it is shown that ethylic oxalacetate is not a salt of keto-succinic acid but of hydroxyfumaric or hydroxymaleïc acid; it therefore has the constitution $COOEt \cdot C(OH) \colon CH \cdot COOEt$.

The salts of succinic, methylsuccinic, and malonic acids all behave optically as if they possessed the constitutions usually assigned to them; no evidence supporting the existence of the tautomeric enolic form sometimes attributed to malonic acid was obtained.

The spectrometric examination shows clearly that the substances hitherto regarded as ethylic acetomalonate, diacetomalonate, and ethylacetomalonate have quite different constitutions. The product of the action of ethylic chlorocarbonate on ethylic sodacetoacetate seems to have the constitution $COOEt \cdot O \cdot CMe \colon CH \cdot COOEt$; it is not identical, but isomeric, with the substance obtained by the interaction of acetic chloride and ethylic sodiomalonate; this has the constitution $OH \cdot CMe \colon C(COOEt)_2$ or $CH_2 \colon C(OH) \cdot CH(COOEt)_2$. The former substance has a neutral reaction and does not colour ferric chloride, whilst the latter is strongly acid and gives an intense coloration with ferric chloride. Ethylic diacetomalonate is dienolic, having the constitution $C(CH_2 \colon C \cdot OH)_2(COOEt)_2$. Further, ethylic ethylacetomalonate contains no ethylenic bond, but has the constitution $CMeO \cdot CEt(COOEt)_2$.

Acetylacetone has the constitution $OH \cdot CMe \colon C \colon CMe \cdot OH$,

$$CH_2 \colon C(OH) \cdot CH_2 \cdot C(OH) \colon CH_2, \text{ or } OH \cdot CMe \colon CH \cdot C(OH) \colon CH_2,$$

and does not seem to become ketonic on heating. Mesitylic oxide and phorone probably have the constitutions $CMe_2 \colon C \colon CMe \cdot OH$ and $CMe_2 \colon C \colon C(OH) \cdot CH \colon CMe_2$ respectively.

The constitution assigned by v. Pechmann to ethylic acetonedicarboxylate is confirmed by the spectrometric results; acetylacetone and ethoxalylacetone are enolic compounds, having constitutions of the form $OH \cdot CMe \colon CH \cdot C(OH) \colon CH_2$ and

$$COOEt \cdot C(OH) \colon CH \cdot C(OH) \colon CH_2$$

respectively.

A spectrometric examination of several oxymethylene and carboxyl-derivatives of camphor and of pyrotritartaric acid was also made; the latter substance would seem to have the constitution assigned to it by Paal and by Knorr, and is not a pentamethylene-derivative as supposed by Fittig. W. J. P.

Line Spectrum of Sulphur. By A. DE GRAMONT (*Compt. rend.,* **119**, 68—71).—The line spectrum of sulphur, which is usually obtained by passing a condensed spark through sulphur vapour under low pressure, can also be obtained much more simply under ordinary pressure by passing a condensed spark between two platinum wires or two carbon rods covered with pure fused and cooled sulphur.

If the condenser is not used the sulphur inflames. Drawings of the spectrum and measurements of the wave-lengths are given. The groups in the red and green have a striated appearance which makes them easily recognisable.

Various natural metallic sulphides, when treated in the same way with a condensed spark, show the sulphur lines, although some of the groups may be masked by the lines proper to the metals present in the sulphides.　C. H. B.

Influence of Sodium and Ammonium Hydrogen Molybdates on the Rotatory Power of Rhamnose. By D. GERNEZ (*Compt. rend.*, **119**, 63—65).—The addition of small quantities of sodium hydrogen molybdate or ammonium hydrogen molybdate to aqueous solutions of rhamnose produces a relatively large increase in the rotatory power. When one-twelfth of a molecular proportion of the molybdate has been added, the observed rotation has nearly double its original value, but beyond this point the addition of further quantities of the salt produces relatively less and less effect. The addition of 6·75/24 of the molecular weight of the salt produces the maximum effect, the rotatory power $[\alpha]_D$ being 22°·95 with sodium hydrogen molybdate, and 19°·91 with ammonium hydrogen molybdate. Further quantities of the salts produce no appreciable change. It is noteworthy that the maximum effect in the case of rhamnose is produced by the same relative proportions of the molybdates as in the cases of mannitol, sorbitol, and perseitol.　C. H. B.

Change of Sign of Rotatory Power. By A. COLSON (*Compt. rend.*, **119**, 65—68).—Pure amylic acetate, after fractionation over acetic anhydride, and the same product mixed with 1 per cent. of the anhydride, give the following rotations at different temperatures.

	−4°.	+16°.	60°.	78°.	100°.
Pure acetate....	0° 53′	1° 2′	1° 20′	1° 24′	1° 20′
Mixture........	1　6	1　4	--	1　8	--

Pure amylic acetate seems to show all the characteristics of the internal congelation described by Le Bel (this vol., ii, 304), but the presence of a small quantity of acetic anhydride neutralises the effects of temperature. In view of the easy decomposition of ethereal salts, it is not improbable that the anhydride, by reason of its power of combining with water, gives stability to the molecule of the acetate, and hence brings about a condition of stable equilibrium in the liquid. This view is supported by the fact that acetylmaleic anhydride, which is both an acetate and an anhydride, shows the following rotations when pure and when mixed with 1 per cent. of acetic anhydride.

	60°.	40°.	30°.	18°.
Pure compound ..	−1° 32′	−1° 22′	−1° 18′	−1° 8′
Mixture	−1　29	−1　21	−1　18	−1　10

It follows that whilst there are compounds which have a rotatory power which varies greatly with the temperature, in some cases these variations are the result of variations in the conditions of chemical equilibrium.　C. H. B.

Variation of Rotatory Power with the Temperature. By A. LE BEL (*Compt. rend.*, **119**, 226—228).—A continuation of the discussion with Colson. The great variations in rotatory power with variations in temperature, observed in the case of methylic and ethylic tartrates, cannot be attributed to the presence of small quantities of tartaric acid and ethylic or methylic alcohol, and Ramsay has shown that at 70° ethylic tartrate consists of simple molecules.

C. H. B.

Gas Batteries. By F. J. SMALE (*Zeit. physikal. Chem.*, **14**, 577—622).—The electromotive force was determined in the case of a large number of gas batteries, the electrode being usually platinum strips coated with platinum black, and immersed partly in the gas, partly in the electrolyte.

Experiments were performed to test the dependence of the E.M.F. on the nature and size of the plates and nature and concentration of the solutions. The nature of the plates had no effect, similar results being obtained with gold, platinum, and palladium, whilst a slight variation with the size, in the case of an oxygen-hydrogen chain, is explained by the slight absorption of oxygen by platinum black. The E.M.F. appeared to be independent of the electrolyte and its concentration, in the case of sulphuric, phosphoric, and chloracetic acids, and also, although less certainly, with sodium and potassium hydroxides, sodium sulphate, and potassium chloride. Abnormal values were, however, obtained with the halogen acids and many salts, which the author accounts for by the existence of secondary actions. Gaseous chains of hydrogen chlorine, hydrogen bromine, and hydrogen iodine were investigated, and the effect of dilution of a gas studied by the comparison of a hydrogen oxygen with a hydrogen air chain, the E.M.F. in the latter case being about 10 per cent. lower. The means of the result for the chains are—hydrogen oxygen, 1·044 volts; hydrogen chlorine, 1·532 volts; hydrogen bromine, 1·111 volts; hydrogen iodine, 0·530 volt. By immersing the electrodes in the same electrolyte at different concentrations, the electromotive force between the two solutions is found, and a number of tables with these results are recorded. The E.M.F. in the oxygen hydrogen chain falls regularly as the temperature increases, thus—0° = 1·090 volts, 20° = 1·065, 40° = 1·033, 60° = 1·001, and from these numbers the temperature coefficient of the solution tension is calculable, giving the result $\frac{d\pi}{dt} = -0·00140$; that is the solution tension is inversely proportional to the absolute temperature. The E.M.F. with the similar electrode in an electrolyte at different temperatures was also observed and calculated, with fair agreement in the results. (See also this vol., ii, 305, 373.)

L. M. J.

Thermoelectric Heights of Antimony and Bismuth Alloys. By C. C. HUICHINS (*Amer. J. Sci.*, [3], **48**, 226—230).—The author has investigated the alloys of bismuth, antimony, and tin with the object of finding the best combination to use for the preparation of thermo-couples. The results show that the best results are obtained

when for the one element is taken bismuth containing 2 to 5 per cent. of antimony, and for the other bismuth with from 5 to 10 per cent. of tin. Both of these alloys are easily cast into very thin leaves, and are sufficiently tough to stand ordinary treatment. A junction of two very thin bars of bismuth with 2 per cent. of antimony, and of bismuth with 10 per cent. of tin gave an E.M.F. of $10700 + 41\,t$ in C.G.S. units.   H. C.

Thermochemical Changes in the Secondary Cell. By F. STREINTZ (*Monatsh.*, **15**, 285—294).—The processes taking place in the secondary cell may be represented symbolically in the following manner.

$$\overset{-}{\text{Pb}} \qquad H_2SO_4 \qquad Aq \qquad H_2SO_4 \qquad \overset{+}{PbO_2}$$
$$PbSO_4 \qquad\qquad Aq \qquad\qquad PbSO_4$$
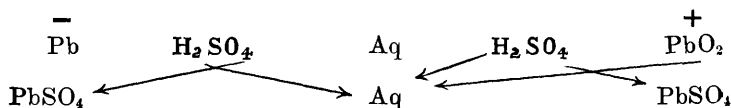
They include the following reactions.

$$H_2O = H_2 + O - 684\,K.$$
$$Pb + O = PbO + 503\,K.$$
$$PbO_2 + H_2 = PbO + H_2O + a\,K.$$
$$PbO + H_2SO_4,Aq = PbSO_4 + Aq + 234\,K.$$
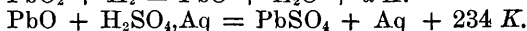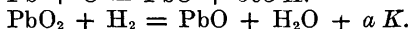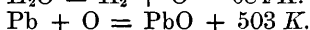
The chemical energy of the cell is obtained by adding these equations.

$$E_c = Pb + 2H_2SO_4,Aq + PbO_2 = 2PbSO_4 + Aq + (a + 287)K.$$
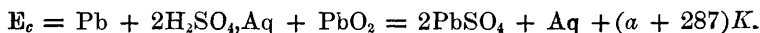
In order to find the value of a, the author selected the reaction

$$PbO_2 + 4HCl + H_2SO_3 + 2H_2O = PbSO_4 + 4HCl + 3H_2O,$$

for thermochemical measurement. This gives

$$PbO_2 + H_2SO_3,Aq = PbSO_4 + Aq + c'\,K,$$
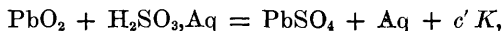
and it can be shown that $a = (103 + c')K$. The value found for c' was $767\,K$, a value which, however, also includes the heat of solution of a small portion of the lead sulphate in hydrochloric acid. From this

$$E_c = PbO_2 + 2H_2SO_4,Aq + Pb = 2PbSO_4 + Aq + 870\,K.$$
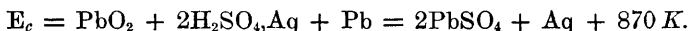
The E.M.F. calculated from this is 1·885 volts, that directly observed being 1·900.   H. C.

Determination of Dielectric Constants. By W. NERNST (*Zeit. physikal. Chem.*, **14**, 622—663).—In the arms AB, AC of a Wheatstone bridge, two adjustable electrolytic resistances are placed; the two arms BC, CD contain two similar condensers consisting of two metal plates separated by a movable glass plate. The ends A, D are connected with an induction coil and B, C to a telephone in which silence or at least a minimum of sound occurs when $R_{ab} : R_{ac} = C_{db} : C_{dc}$. A condenser consisting of a nickel or platinum trough with a fixed metal plate in the interior can be placed in either arm DB or

DC, and its capacity added to either of the measuring condensers, and this contains the liquid whose dielectric constant is to be measured. Minimum sound is then obtained by moving the glass of the measuring condenser. The arms DB, DC contain also auxiliary resistances, so that if the compound examined is not a perfect insulator its resistance can be also determined, since a minimum also results when $R_{ab} : R_{ac} = R_{db} : R_{dc}$. The condensers and other parts of the apparatus are calibrated once for all, and full details of the precautions, and a discussion of the probable errors, are given in the paper. The availability of the method is well seen by comparing the numbers which the authors obtained with it, and the determinations made by Landolt and Jahn (Abstr., 1893, ii, 57). In the case of 13 hydrocarbons, the mean difference is about 2 per cent., the results by this method being in almost all cases the higher. A number of measurements of the capacity of benzene, aniline, amylic alcohol, ethylic alcohol, and water at varying temperatures are also recorded; from the results, the temperature coefficients are calculated; the dielectric capacity in each case decreasing with increasing temperature.   L. M. J.

The Influence of Pressure on the Conductivity of Electrolytes. By I. FANJUNG (*Zeit. physikal. Chem.*, **14**, 673—700).—The work of previous observers, especially Fink's, had shown that in the case of strongly dissociated compounds pressure affects the conductivity, probably owing chiefly to the alteration in the velocity of the ions. The author extends the observations to slightly dissociated compounds, and determines the conductivity of various organic acids and salts at concentrations varying from 1 to 1024 litres of solvent per gram molecule of dissolved substance, and at pressures varying from 1 to 260 atmospheres. The compounds examined were formic, acetic, propionic, butyric, isobutyric, lactic, succinic, malic, benzoic, and hydrochloric acids, and their sodium salts. In *all* cases, pressure caused a decrease in the electrical resistance, the alteration at 260 atmospheres varying from 6·55 to 9·02 per cent. in the organic acids, and from 1·23 to 2·92 per cent. in the more strongly dissociated compounds, corrections having been made for the compressibility of the solution. The rate of increase in conductivity is not constant; in most cases it decreases with increasing pressure. In the highly dissociated compounds, the alteration is most probably due to the diminution of the internal friction (see also this vol., ii, 410), and as the alteration of the fluid friction of water (1·2 per cent. at 260 atmos.) is comparable with the change in resistance of those solutions, it appears that an alteration of internal friction of the solvent is associated with an approximately equal alteration in the ionic friction. The value of μ_∞ for the various pressures is also calculated, and hence by aid of the equations $\mu^2/\mu_\infty(\mu_\infty-\mu)v = K$, and $100 \, RTd \, \log. \, K/dp = \Delta v$, the volume alteration Δv, due to dissociation, can be deduced. This is done for the acids considered, and the results compared with those obtained by subtracting the volume increase on neutralisation from that obtaining with hydrochloric acid, the agreement of the results being remarkably close.   L. M. J.

Decrease of Conductivity when the Water of Solution is displaced by Alcohol. By C. SCHALL (*Zeit. physikal. Chem.*, **14**, 701—708).—The conductivity of aqueous solutions of electrolytes is lowered by the addition of a non-electrolyte such as alcohol (Abstr., 1892, 1038) but to varying extents, hence acids at concentrations at which the conductivity is equal in aqueous solution give unequal values in alcoholic solutions. This is proved in the case of hydrochloric, picric, oxalic, and dichloracetic acids, the conductivities of which were determined in solutions in water, methylic alcohol and dilute ethylic alcohol. If the velocity of the hydrogen ion greatly exceeds that of the combined ion, then, the author considers, the alteration is due chiefly to the change in degree of dissociation of the compound, which must, therefore, be widely different in alcoholic solutions at concentrations at which the dissociation degrees in water are equal. L. M. J.

Specific Heat of Liquid Sulphurous Anhydride. By E. MATHIAS (*Compt. rend.*, **119**, 404—407).—The specific heat of liquid sulphurous anhydride has been directly measured by the author, at temperatures varying from −20° to 155·5°. He finds that the true specific heat of the liquid is always positive and increases with the temperature. Between −20° and +130° the specific heat m is given approximately by the formula

$$m = 0·31712 + 0·0003507t + 0·000006762t^2.$$

H. C.

Heat of Fusion of some Organic Compounds. By L. BRUNER (*Ber.*, **27**, 2102—2107).—This has been determined for the compounds mentioned below; the results of individual experiments never differed by more than 2—3 per cent. The numbers indicate the Calories given out by 1 gram of the substance on solidifying; those in brackets indicate the heat of fusion as calculated by van't Hoff's formula from the lowering of freezing-point caused by the same substance. It will be noticed that the heat of fusion of a bromo-derivative is less than that of the mother substance, or of the analogous chloro-derivative.

Methylic oxalate, 42·6. Crotonic acid, 25·3. Phenylacetic acid, 25 4 Bromal hydrate, 16·9. Stearic acid, 47·6 (49·2). Palmitic acid, 39·2 (49·5). Paradichlorobenzene, 29·9. Paradibromobenzene, 20·6. Metachloronitrobenzene, 29·4. Parachloronitrobenzene, 21·4. Orthonitrophenol, 26·8. Paracresol, 26·3 (26·0). Azoxybenzene, 21·6. Azobenzene, 27·9 (28·2). Parachloraniline, 37·2. α-Naphthylamine, 22·3 (26·3). Benzophenone, 23·7 (21·5). Menthol, 18·9.

C. F. B.

The Function a in Van der Waals' Equation. By G. BAKKER (*Zeit. physical. Chem.*, **14**, 664—670).—From thermodynamical equations is deduced the conclusion that the function a in van der Waals' equation decreases with increase of temperature until a zero value is reached, and that the curve which expresses the relation of this function to the temperature is convex to the axis of temperature. The author points out further that these results are also proved by the

experimental observations, or at least are valid in the cases of hydrogen and carbonic anhydride.   L. M. J.

Relations between the Laws of Mariotte, Gay Lussac, and Joule. By G. BAKKER (*Zeit. physikal. Chem.*, **14**, 671—672).—Owing to a statement in Poincaré's "Cours de physique mathématique," that Joule's law does not follow necessarily from the other two laws, the author reduces the expressions to the following forms:—

Boyle's law, $pv = f_1(T)$; Gay Lussac's law, $\epsilon + pv = f_3(T)$; Joule's law, $\epsilon = f_2(T)$, in which case either follows as a necessary consequence from the other two.   L. M. J.

Gas Baroscope and its Applications. By G. BODLÄNDER (*Ber.*, **27**, 2263—2270, and *Zeit. angw. Chem.*, **14**, 425—431).—The determination of the weight G of a gas is usually made indirectly by measurement of the volume V at the atmospheric pressure b and temperature t. If M is the molecular weight of the gas, then 1 c.c. weighs 0·0446725 M and

$$G = \frac{V \times b \times 273 \times 0\cdot0446725 \times M}{(1 + 0\cdot0001614t) \times 760 \times (273 + t)} \text{ milligrams.}$$

Instead of varying the volume and pressure of the gas, it would be simpler, both for measurement and calculation, to bring the volume of the gas, by either compression or expansion, always to some constant quantity, so that the pressure alone would vary and be proportional to the amount of the gas. If the constant volume V is so selected that

$$V = \frac{(1 + 0\cdot0001614t) \times 760 \times (273 + t)}{273 \times 0\cdot0446725 \times 100} \text{ c.c.}$$

then $$G = \frac{b\,M}{100} \text{ milligrams.}$$

The gas baroscope is an instrument constructed on the above principle. It consists of a glass globe, closed above by a three-way stopcock, and terminating below in a graduated tube which communicates with a mercury reservoir. The volumes of the globe and tube are so selected that the graduations give the values of V for temperatures varying from 0° to 30°, as calculated from the equation given above. The gas to be examined is introduced into the globe, and the height of the mercury in the reservoir so adjusted that its level in the graduated tube corresponds with the temperature of the gas. The gas is then expelled from the globe, which now remains vacuous, and the height of the mercury again adjusted so that the level of the mercury in the graduated tube is that maintained in the previous measurement. The difference between the heights of the mercury in the two cases gives the value of b, and G is then easily calculated. The gas baroscope may be used in all cases in which the weight of a gas has to be ascertained. Experiments are detailed in the papers in which it has been applied to the determination of nitrogen by Dumas' method, to the measurement of vapour densities, and to the

analysis of substances, such as carbonates and nitrates, which give rise to gaseous products of decomposition (see this vol., ii, 471).

H. C.

Relation between the Density of a Saline Solution and the Molecular Weight of the Dissolved Salt. By G. CHARPY (*Compt. rend.*, **119**, 156—158).—In a previous paper (Abstr., 1892, 765), in studying the densities of saline solutions, the author represents the concentration by the ratio of the number of molecules of the dissolved compound to the total number of molecules of the solution. The molecular weight of water was then taken as 18, but as Ramsay's recent investigations lead to the conclusion that the liquid molecule of water is greater than the gaseous molecule, the author has now recalculated his results, using in the one case 3×18, and in the other 4×18, as the molecular weight of water. He finds that for values very little higher than 3×18, the curves representing the densities plotted against the concentrations become straight lines, or in other words, if it is assumed that at $0°$ the molecular weight of water is about 3×18, the density of a saline solution is found to be proportional to the molecular concentration.

With the aid of this new and simple relationship, the question of the connection between the density of a saline solution and the molecular weight of the dissolved salt was further studied. A number of sulphates and chlorides were examined, and it was found that the densities of solutions of the same concentration (molecular) are in the case of analogous salts proportional to the molecular weights of these salts.

H. C.

Density of Dilute Aqueous Solutions. By F. KOHLRAUSCH and W. HALLWACHS (*Ann. Phys. Chem.*, [2], **53**, 14—42).—In order to determine the densities of dilute aqueous solutions to within a limit of error of 10^{-6}, the authors have had recourse to the displacement method of weighing a ball of glass in the liquid under examination. The ball is suspended from an arm of the balance by means of a single cocoon fibre; its total weight was 133 grams, but when weighed in the solutions under examination its weight never exceeded 4 grams. In this way solutions of densities up to $1·03$ could be examined. Great care was taken in measuring the temperature and in maintaining it constant during the carrying out of a determination, a greater variation than $\frac{1}{100}°$ being in no case allowed. A precise description of the apparatus employed for this purpose and its mode of arrangement is given in the paper.

Determinations were made with solutions of sodium chloride and carbonate, magnesium and zinc sulphates, hydrochloric, sulphuric, phosphoric, tartaric, acetic, and monochloracetic acids, and cane sugar. Tables are given of the results obtained in each case. By combining the results with those obtained for concentrated solutions of the compounds examined by Gerlach, Marignac, Oudemans, and Kohlrausch, complete density tables for solutions of these compounds are obtained. From these, the molecular volumes ϕ of the dissolved substances are calculated, on the assumption that the water undergoes no contraction in volume. The molecular volumes are found to

increase regularly with the molecular concentration, except in solutions containing less than $\frac{1}{2}$ gram-mol. per litre of zinc and magnesium sulphates, sulphuric, phosphoric, tartaric, and monochloracetic acids. With dilute solutions of these compounds, the molecular volume at first increases very rapidly, and it is only when the concentration exceeds that named, that the regular increase of the molecular volume with the concentration is observed. H. C.

Viscosity of Solutions. By G. Jäger (*Monatsh.*, **15**, 254—268). —The coefficient of viscosity μ may be expressed by the formula $\mu = 2\rho r^2 c/3\lambda$, where r is the radius, c the velocity, λ the mean length of the path of a molecule, and ρ the density of the solution. If v is the volume of the liquid under consideration, and b the space in the volume v actually filled with matter, the above expression becomes

$$\mu = \frac{4r\rho c}{9\left(1 - \sqrt[3]{\dfrac{b}{v}}\right)}.$$

The coefficient of viscosity is also a function of the temperature $\mu = f(t)$, so that the coefficient of a solution that has a melting point reduction Δ, is $\mu_\Delta = f(t + \Delta)$. Developing according to Taylor's theorem $\mu - \mu_\Delta = -\Delta f'(t) - \dfrac{\Delta^2}{2} f''(t) - \ldots$. For water, the values of the function and its derivatives are calculated empirically from the experiments of Sprung, and the formula is then applied to aqueous solutions. The calculated results are found to be in general agreement with those obtained experimentally by Sprung. H. C.

Saturated Solutions. By A. Étard (*Ann. Chim. phys.*, [7], **2**, 503—574; compare Abstr., 1892, 398).—Determinations of the solubility of salts between 100° and 250° are conveniently made in a glass tube bent at 120° and constricted at the middle. The salt is placed in one arm, and the tube partly filled with water and sealed off; after heating, at a fixed temperature, in a bath containing a molten mixture of potassium and sodium nitrates, part of the solution is caused to run into the second arm of the bent tube, and is analysed when cold. Solubilities at temperatures above 250° are best determined by Guthrie's method.

The solubility, y, of a salt is taken by the author as the percentage of salt contained in the saturated solution; if p be the weight of salt, and $p + \pi$, the weight of solution in which it is contained, then $y = \dfrac{100p}{p + \pi}$. Using this scale of solubilities in place of the ordinary one, the curve connecting solubility and temperature lies wholly between 0 and 100 per cent. of salt; further, 100 on the y-axis corresponds with the melting point of the anhydrous salt on the other axis; the curve is also a curve of melting points of mixtures of dissolved substance and solvent.

The experimentally determined solubility curves usually consist first of a curved part, of which the continuation is one or more straight lines; the last of these passes through the " limiting " point,

or point of fusion of the anhydrous substance. The second column in the following table gives the equation to these straight line solubility curves, and the third column $(t_1 - t_2)$ gives the limits of temperature between which the equations hold; the solvent used was water.

Salt.	y.	$t_1 - t_2$.
AgNO$_3$	$81{\cdot}5 + 0{\cdot}1340t$	60—$198°$
KNO$_3$	$24{\cdot}0 + 0{\cdot}7100t$	20—70
	$59{\cdot}5 + 0{\cdot}3727t$	70—125
	$80{\cdot}0 + 0{\cdot}0938t$	125—338
NaNO$_3$........	$39{\cdot}0 + 0{\cdot}2825t$	-5—$+64$
	$58{\cdot}5 + 0{\cdot}1666t$	64—313
Ba(NO$_3$)$_2$......	$4{\cdot}5 + 0{\cdot}2025t$	$0{\cdot}4$—475
KClO$_3$	$2{\cdot}5 + 0{\cdot}2060t$	0—50
	$12{\cdot}7 + 0{\cdot}4230t$	50—150
	$55{\cdot}0 + 0{\cdot}2163t$	150—358
Ba(ClO$_3$)$_2$	$19{\cdot}0 + 0{\cdot}382t$	0—100
KCl	$19{\cdot}6 + 0{\cdot}1916t$	-11—$+25$
	$26{\cdot}5 + 0{\cdot}1039t$	25—732
NaCl	$25{\cdot}8 + 0{\cdot}0248t$	0—250
	$a + \alpha t$	250—772
BaCl$_2$	$25{\cdot}5 + 0{\cdot}1074t$	0—93
	$35{\cdot}5 + 0{\cdot}0600t$	93—215
KBr	$28{\cdot}2 + 0{\cdot}2700t$	-20—$+38$
NaBr	$40{\cdot}1 + 0{\cdot}1314t$	-22—$+51{\cdot}5$
	$49{\cdot}5 + 0{\cdot}0690t$	$51{\cdot}5$—230
KI	$57{\cdot}0 + 0{\cdot}1090t$	0—111
	$68{\cdot}5 + 0{\cdot}0618t$	111—638
NaI	$59{\cdot}5 + 0{\cdot}1933t$	-5—$+60$
	$74{\cdot}0 + 0{\cdot}0450t$	70—$626°$
CdI$_2$	$42{\cdot}4 + 0{\cdot}1154t$	-4—$+97$
	$55{\cdot}0 + 0{\cdot}1076t$	97—366

The solubility curve of silver nitrate is a curved line between -7 and $+60°$, whilst the curve for potassium nitrate is slightly curved between $-3°$ and $+20°$.

In addition to the above, the author has determined the solubilities of a large number of other salts, for which the original paper must be consulted. The solubility curves of mercuric chloride in water and in 13 organic solvents were determined; those for cupric chloride in 9 organic liquids. In these cases, just as in those of aqueous solutions, the solubility curves are composed of straight lines, the last of which points towards the melting point of the salt; evidence of the existence of numerous double compounds of these two chlorides with the solvent was obtained.

The curves of solubility of sulphur in carbon bisulphide, benzene, and ethylenic dibromide extend from the freezing point of the solvent to the melting point of sulphur. The solubility of sulphur in hexane was also determined. **W. J. P.**

Solubility of Inorganic Salts in Organic Solvents. By S. v. LASZCZYNSKI (*Ber.*, **27**, 2285—2288).—The author gives tables of the solubilities of copper chloride, mercuric chloride, mercuric iodide, cobalt chloride, stannous chloride, lithium chloride, lead iodide, potassium iodide, silver iodide, silver nitrate, bismuth nitrate and potassium thiocyanate in ethylic ether, ethylic acetate, acetone, amylic alcohol, benzene, aniline, and pyridine.   E. C. R.

Change of Free Energy on mixing Concentrated Solutions. By W. NERNST (*Ann. Phys. Chem.*, [2], **53**, 57—68).—The author shows that when two concentrated solutions of similar composition, but of different concentration, are mixed, the heat which is developed is generally a measure of the energy set free, or that generally the change in free energy is equal to the change in the total energy of the system. Thus, if the vapour pressures of the two solutions at the absolute temperature T are p_1 and p_2, in order to transfer 1 gram mol. of water from the one solution to the other, the work required will be $RT \log \frac{p_2}{p_1}$, where R is equal to 2·00 if the work is expressed in gram-calories. This quantity should, according to the rule given above, be equal to the difference in the heats of dilution of the two solutions, if their concentrations only differ by the gram-molecule of water transferred. This is shown to be the case with certain solutions of sulphuric acid.   H. C.

Endothermic Reactions effected by Mechanical Force. By M. C. LEA (*Zeit. anorg. Chem.*, **7**, 50—51).—Referring to Spring's claim of priority (this vol., ii, 275), the author maintains that neither Spring nor anyone else had shown the carrying through of a truly endothermic reaction (that is, one requiring the continual supply of energy during the whole reaction, and not only for the starting of the reaction) by purely mechanical means, and so maintains his own claim to priority.   L. T. T.

Endothermic Reactions effected by Mechanical Force. By W. SPRING (*Zeit. anorg. Chem.*, **7**, 51)—A reply to M. C. Lea (see preceding abstract), maintaining his former claim.
        L. T. T.

Apparatus for Facilitating the Boiling of Liquids. By V. GERNHARDT (*Ber.*, **27**, 2640—2641 ; compare this vol., ii, 268).—The apparatus in question is identical with Beckmann's (D.R.P. 53,217).   M. O. F.

Apparatus for Continuous Evolution of Gas. By N. TECLU (*Zeit. anal. Chem.*, **35**, 441—446).—This is a modification of Ostwald's hydrogen sulphide apparatus (Abstr., 1893, 268).   M. J. S.

Improved Drying Oven. By W. HOFFMEISTER (*Zeit. anal. Chem.*, **35**, 437—438).—The oven is designed for drying substances in a current of illuminating or other gas, or under reduced pressure.

The form is that of the ordinary rectangular chest, but the door is made to close air-tight. The gas with which it is to be filled is introduced by a copper spiral pierced with numerous holes. Openings at the top of the chest allow of the insertion of a thermometer and a tube, by which connection may be made either with the burner which is to consume the gas after passing through the oven, or with a pump, by which, when the inlet tube is closed, the pressure in the interior may be lowered. M. J. S.

Inorganic Chemistry.

Preparation of Chlorine for Laboratory Purposes. By F. A. GOOCH and D. A. KREIDER (*Zeit. anorg. Chem.*, **7**, 17—21).—When hydrochloric acid of sp. gr. 1·1, heated to about 80°, is allowed to come slowly in contact with pieces of potassium chlorate which have been previously fused, a steady evolution of gas takes place. Under these conditions, about 82—85 per cent. of the gas is chlorine, the remainder being chlorine dioxide. Another 10 per cent. of the dioxide may be decomposed by passing the evolved gas through a saturated hydrochloric acid solution of manganous chloride at 90°. If the gas is wanted absolutely pure, the gas, after passing through the manganous chloride, may be passed through a combustion tube filled with asbestos and heated to redness. Care must be taken to have the acid hot, and not to allow the action to become rapid, or the proportion of chlorine dioxide may become much increased and explosion occur. 1 gram of potassium chlorate yields about half a litre of chlorine.

If a Kipp or some similar constant gas generating apparatus is employed, and the acid heated by a steam jacket or by standing the generator in hot water, this method forms a convenient constant chlorine apparatus for laboratory use. L. T. T.

The Condition of Iodine in Solution, and the probable Cause of the different Colours of its Solutions. By G. KRÜSS and E. THIELE (*Zeit. anorg. Chem.*, **7**, 52—81; compare Gautier and Charpy, Abstr., 1890, 446).—The authors detail numerous determinations of the molecular weight of iodine in solution, and also of its absorption spectra in 34 solvents (in each case at two temperatures).

Although the boiling and freezing point experiments negative the existence of complex chemical molecules of iodine, the authors believe that they do not disprove the possibility of complex " physical molecules " or groups of molecules. The experiments of Anschütz, Behrend, and others on the freezing points of solutions of naphthalene and picric acid in benzene and chloroform, of phenanthrene picrate in alcohol, &c. (where figures are obtained such as would be expected

if the molecule had beccme dissociated whilst other evidence is against such dissociation), points to the possibility of the existence of such loosely bound groups of molecules without their being detected by the Raoult method. Determinations of the molecular weight of anthracene picrate in benzene made by the authors, both by the boiling point and freezing point methods, gave half the true molecular weight, or results such as would be expected if dissociation had occurred, whilst the dark red colour of the solution showed that such dissociation had not taken place.

The behaviour of iodine in its compounds also points to a tendency to form molecular aggregates. Thus the polyiodides all contain I_2, or a multiple thereof, and never an uneven number of iodine atoms in excess of those in the simple iodide.

The authors conclude that the fundamental colour is dependent on the aggregation of the molecules of the iodine. In the brown solutions, the dissociating power of the solvent is not sufficient to overcome the aggregating tendency of the iodine molecule, and the iodine is in the form of $[I_2]_n$, whilst in violet solutions the iodine exists in its simple form of I_2. This would also account for the fact that brown iodine solutions tend, when heated, to pass into violet, and violet solutions when much cooled to change to brown. It is probable that the refractive and dispersive powers of the solvent may also have its influence in displacing the absorption bands, and that some of the variations in shade of the solutions may be due to this cause.   L. T. T.

Action of Reducing Agents on Iodic acid. By Miss C. F. ROBERTS (*Amer. J. Sci.*, [3], **48**, 151—158).—Most text books state that nitric oxide is absorbed by aqueous iodic acid with liberation of iodine, but of the character and degree of ease of the reaction little is known. The authoress finds that nitric oxide causes no appreciable separation of iodine from dry iodic acid, or from solutions of that acid in sulphuric acid. Nitric oxide is, however, absorbed by aqueous solutions of iodic acid of any strength, but the reaction takes place slowly even when the gas is confined over the acid, and not at all when the gas is merely passed rapidly through the solution.

When potassium iodide is added to dilute solutions of iodic acid, or of hydrochloric acid, ro iodine is separated ; but when a solution of potassium iodide is gradually added to a mixture of weak solutions of iodic and hydrochloric acids, the solution becomes yellow, then orange, and, finally, particles of iodine separate. The iodine could not be detected by the starch reaction, as iodine monochloride is one of the products first formed. When iodic acid is in excess, the reaction takes place according to the equation $HIO_3 + 2KI + 5HCl = 3H_2O + 2KCl + 3ICl$. Part of the iodine monochloride is subsequently decomposed with liberation of iodine. Other reducing agents, such as sodium thiosulphate, arsenious anhydride, ferrous sulphate, stannous chloride, potassium thiocyanate, and nitric oxide produce similar effects.

Although a solution of iodine in iodic acid turns starch blue, as does also one of iodine in hydrochloric acid, yet, if the two solutions be

mixed, the starch immediately loses its blue tint, but regains it on the addition of an alkali carbonate. The proportions in which iodic acid and iodine were found to react in presence of hydrochloric acid were as 1 : 4. The reaction takes place according to the equation

$$HIO_3 + 2I_2 + 5HCl = 3H_2O + 5ICl.$$

It is probable that the action of potassium iodide or other reducing agent on iodic acid in presence of hydrochloric acid is first to liberate iodine, which at once acts on the mixture of the two acids to form iodine monochloride. It could not be ascertained whether the first action on the iodic acid was to form a higher oxide (I_2O_7) or a lower (I_2O_4). Whichever is the case, the mixture of iodine and iodic acid, both ordinarily oxidising agents, is able to effect the decomposition of hydrochloric acid with formation of iodine monochloride. L. T. T.

Ozonising Apparatus. By H. N. WARREN (*Chem. News*, **70**, 41—42).—Pieces of tinfoil, in close proximity to one another, are attached to the inner surface of glass tubes (similarly to the diamond Leyden jar), and can then be used for ozonising air or oxygen, in place of the usual apparatus. D. A. L.

Influence of Pressure on the Combination of Hydrogen with Selenium. By H. PÉLABON (*Compt. rend.*, **119**, 73—75).—When selenium is heated at 620° with hydrogen in sealed tubes in which the pressures are respectively 520 mm., 1270 mm., 1520 mm., and 30,160 mm., the values obtained for the ratio of the partial pressure of the hydrogen selenide to the total pressure are 0·405, 0·4112, 0·42, and 0·423 respectively. At 575°, for pressures of 678 mm. and 1380 mm., the ratios were 0·39 and 0·403 respectively. At a much lower temperature, namely, 310°, and pressures of 580 mm. and 1520 mm., the ratios were 0·214 and 0·23 respectively. It follows that, as Ditte has already observed, an increase of pressure increases very slightly the quantity of hydrogen selenide produced at a given temperature, and the effect of pressure is less the higher the temperature. This result is in agreement with the ordinary theory of dissociation.

The author finds that increase of pressure increases the rate of formation of the hydrogen selenide. C. H. B.

Action of Chlorine on Phosphonium Iodide. By J. C. CAIN (*Chem. News*, **70**, 80—81).—By the action of chlorine or phosphorus pentachloride on phosphonium iodide, a mixture of amorphous phosphorus and solid hydrogen phosphide is obtained. D. A. L.

Bromoborates. By G. ROUSSEAU and H. ALLAIRE (*Compt. rend.*, **119**, 71—73 ; compare this vol., ii, 413, and Abstr., 1893, ii, 518).—The action of bromine on a mixture of a metal with boronatrocalcite yields a series of bromoborates analogous to the chloroborates previously described (*loc. cit.*). Heintz's method, which in the case of chloroborates is satisfactory only for the zinc salt, is, in the case of bromoborates, satisfactory only for the zinc and magnesium compounds.

The *bromoborates* have the general formula $6M''O,8B_2O_3,M''Br_2$, and crystallise in cubes, tetrahedra, and dodecahedra, which act on polarised light, and seem to have only a pseudocubic symmetry. The magnesium, zinc, cadmium, and manganese compounds are colourless; the cobalt compound is green by transmitted light, and violet by reflected light; the nickel compound is yellow.

In all cases where the bromoborate has been prepared from boronatrocalcite, it contains about 1 per cent. of calcium.

C. H. B.

Behaviour of Sodium Peroxide towards Alcohol. By J. TAFEL (*Ber.*, **27**, 2297—2306; see also this vol., ii, 233).—A compound of the composition NaO_2H, which the author names *sodyl-hydroxide*, is obtained when sodium peroxide is shaken with well cooled absolute alcohol. It remains undissolved as a yellowish sandy mass, whilst the alcoholic solution contains only traces of active oxygen. It dissolves in water with a much smaller development of heat than sodium peroxide, and, when heated in a tube, explodes with evolution of oxygen. It also slowly gives off oxygen at $0°$, absorbs water from the air, and is converted by dry carbonic anhydride into sodium carbonate, water, and oxygen. It dissolves in ice-cold water without evolution of gas, but a slight rise of temperature determines decomposition; when mixed with dilute alcohol, it yields crystals of the compound $Na_2O_2,8H_2O$; with alcoholic hydrogen chloride at $-5°$, it yields a product which contains 1 mol. NaCl and 1 mol. NaO_2H; at higher temperatures the products of the action are sodium chloride and hydrogen peroxide. It dissolves in cold alcoholic acetic acid, and forms a compound of the formula $NaC_2H_3O_2,NaOC_2H_3O_2,H_2O$. With benzoic chloride at ordinary temperatures, it yields sodium chloride and benzoic peroxide (m. p. 105°).

E. C. R.

Preparation of Ammonium Nitrite. By S. P. L. SÖRENSEN (*Zeit. anorg. Chem.*, **7**, 33—40).—The author employs a modification of Erdmann's method. The mixture of nitrogen oxides evolved during the action of arsenious anhydride on nitric acid is passed over coarsely powdered ammonium carbonate kept cool by ice. The half liquid mass is treated with alcohol, the unchanged carbonate filtered off, and the ammonium nitrite precipitated by the addition of ether. The nitrite so obtained is of 90—94 per cent. purity, and may be purified by re-solution in 96 per cent. alcohol and reprecipitation with ether.

Pure ammonium nitrite forms almost colourless needles which are deliquescent, and dissolve in water with development of heat. It is easily but slowly soluble in alcohol, and is precipitated from this solution by ether, chloroform, and ethylic acetate. Concentrated solutions appear to decompose with explosive force at 60—70°, like the solid salt, and in acid solutions such decomposition sometimes occurs at ordinary temperatures. The dry salt may be safely kept in an atmosphere of hydrogen, and in presence of pieces of ammonium carbonate and of lime. It is best kept and transported under absolutely dry and alcohol-free ether.

L. T. T.

Preparation of Potassium Mercuric Iodide. By E. G. Clayton (*Chem. News*, **70**, 102).—Potassium mercuric iodide is readily obtained from ordinary Nessler solution by concentration and crystallisation. D. A. L.

Molecular Weight of Mercurous Chloride. By M. Fileti (*J. pr. Chem.*, [2], **50**, 222—223).—A propos of the paper of Harris and V. Meyer on this subject (this vol., ii, 353), the author calls attention to the fact that, already in 1881, he had determined the vapour density of mercurous chloride, by V. Meyer's method, in an atmosphere of mercuric chloride, and found it to correspond with HgCl (*Gazzetta*, **11**, 341). That no dissociation had taken place was proved by the fact that a cooled gold surface, immersed in the mixed vapours at 400°, received no deposit of mercury. C. F. B.

Separation of the Rare Earths. By H. A. Rowland (*Chem. News*, **70**, 68—69).—The author, like other investigators, finds cerium, lanthanium, praseodymium. neodymium, and thorium differ from the yttrium group, and confirms the occurrence of all these earths, in varying proportions, in such minerals as gadolinite, samarskite, yttrialite, cerite, &c., but adds, that besides the elements of the cerium group, there are at least seven other substances, which he refers to as *a, b, i, d, h, n, c, k*. These are separated from the cerium group by fractionating with sodium sulphate. The mixed earths are dissolved in a slight excess of nitric acid, the solution diluted and kept warm while solid sodium sulphate is stirred in, during a day or two, until the absorption lines of neodymium, the most persistent of the group, disappears from the solution. The precipitate is treated with potash, and the resulting oxides submitted to the same course of treatment, which is repeated a dozen times. The substances *a, b, d, i* appear in the early solutions; *d, n, c*, &c., in the later ones, and can be obtained fairly free from *a, b*, and *i*; but *d* persists throughout, even in the precipitate of the cerium group. Samarskite, as compared with gadolinite, not only contains more of the mixture *d, n,* &c., but also a larger number of elements, one of them being the author's *h*. The sulphates of sodium and potassium each exhibit varying degrees of activity towards these different substances, moreover, the oxalates differ in solubility, but not sufficiently to permit of effective separation. The author has separated *a* from the others in the following manner:—The solution from the sulphate fractionation is slightly acidified with nitric acid, diluted, and treated with weak potassium ferrocyanide solution, at intervals of an hour or so, until cerium bands are no longer visible from 3 inches of the strong solution. The earth is then precipitated as oxalate, and may be obtained quite pure by this method, which, however, only serves for the isolation of *a*. *a* is the principal element of, and has the properties of yttrium, and both the oxalate and oxide are white.

The mixture of *b, i, d* gives cerium absorption and emission bands, but of the former many seem to belong to *b* rather than to *i*. The oxalate of this mixture is red, and the oxide white. *b* is strong in

gadolinite and weak in samarskite. The spectrum of the author's erbium indicates the presence of a fourth constituent.

Substance d has not been isolated, but has, nevertheless, been named demonium, on account of its ubiquity and persistency; a is the only one of these substances obtained free from it. The principal spectrum line of d is at wave-length 4000·6 nearly. The substances n, k, c have a feeble absorption spectrum in the visible spectrum, and a strong one in the ultra violet. Of h, no properties have been ascertained.   D. A. L.

Separation of the Rare Earths. By W. CROOKES (*Chem. News*, **70**, 81—82).—It is pointed out that Rowland's substances, a, b, i, &c. (preceding abstract), are probably already known by accepted names; that white yttrium oxalate and oxide are far from novelties, and that the erbium known to chemists generally, retains its white oxalate, its rose oxide, and a number of bands in its absorption spectrum even after its various acknowledged constituents have been separated.   D. A. L.

Impurities in Aluminium. By H. MOISSAN (*Compt. rend.*, **119**, 12—15).—The usual impurities in commercial aluminium are iron, derived from the raw materials and from the electrodes, and silicon, derived partly from the electrodes and the crucible, but chiefly from the alumina. There is no evidence, in many cases, that silicon has any injurious effect, but it can be partially removed by melting the metal under a layer of an alkali fluoride. In addition to these two impurities, aluminium contains a small quantity of nitrogen, which is evolved as ammonia when the metal is dissolved in potassium hydroxide, and a small quantity of carbon, which remains as a maroon coloured, amorphous residue, quite free from graphite, when the metal is heated with gaseous hydrogen chloride or hydrogen iodide free from oxygen and the greyish residue is treated with dilute hydrochloric acid. The nitrogen is probably present in the form of aluminium nitride; it slightly reduces the breaking strain, the elongation, and the limit of elasticity. The carbon has a much more marked effect in reducing both the breaking strain and the elongation.

Commercial aluminium also contains a small quantity of amorphous alumina, and sometimes small crystals of carbon boride.   C. H. B.

Aluminium Carbide. By H. MOISSAN (*Compt. rend.*, **119**, 16—20).—Aluminium carbide, C_3Al_4, is obtained (1) by heating aluminium in carbon dishes, in the electrical tube-furnace, with a current of 300 ampères and 65 volts, a current of hydrogen being passed through the tube; (2) by heating the metal in a carbon crucible in the electrical furnace, the product in this case being contaminated with nitrogen; or (3) by reducing a mixture of kaolin and carbon in the electrical furnace. In order to remove the excess of metal, the product is treated with concentrated hydrochloric acid at a low temperature, washed rapidly with water, and finally with alcohol.

Aluminium carbide forms transparent, yellow crystals. sometimes 5—6 mm. long; sp. gr. = 2·36. Some have the form of regular hexagons. It is decomposed at the highest temperatures of the electric arc; chlorine attacks it at a dull red heat, with incandescence, aluminium chloride volatilising, and a residue of amorphous carbon, without any trace of graphite, being left; bromine has no action at the ordinary temperature, but attacks the carbide, with incandescence, at about 700°; iodine seems to have no action, even at a bright red heat. Oxygen attacks the carbide superficially only at a dull red heat, whereas at the same temperature sulphur attacks it readily, with great development of heat, and formation of aluminium sulphide and traces of carbon bisulphide, although the greater part of the carbon remains in the form of thin lamellæ Nitrogen and phosphorus have no action on the carbide at a dull red heat, but certain oxidising agents attack it readily. When slightly heated with dry potassium permanganate, it is oxidised with vivid incandescence; potassium dichromate and chromic anhydride oxidise it slowly at dull redness.

The carbide reduces lead peroxide and the red oxide with incandescence, but it is not attacked by potassium chlorate or nitrate. A solution of an alkali dichromate acidified with sulphuric acid attacks it slowly in the cold, or when boiled; fuming nitric acid is without action, even on heating, but on the addition of water the carbide is rapidly attacked; concentrated hydrochloric acid attacks it very slowly, but the dilute acid dissolves it in a few hours; boiling concentrated sulphuric acid is reduced, with formation of sulphurous anhydride, and the dilute acid reacts at about 100°. Fused potassium hydroxide attacks the carbide with great energy at about 300°, but alkali carbonates, even at a bright red heat, produce only incomplete decomposition.

When the carbide remains in contact with water at the ordinary temperature, decomposition takes place very slowly, with liberation of methane and formation of aluminium hydroxide, the change being accelerated by heat, but not appreciably influenced by light.

C. H. B.

Behaviour of Various kinds of Glass with Reagents. By F. FOERSTER (*Zeit. anal. Chem.*, **35**, 381—396).—Out of 14 varieties of glass, all of high repute for chemical purposes, the borosilicate Jena glass, 59 III, and the hard zinc-aluminium-sodium glass (Jena, 165 III) are much less attacked by water at 20° or 80° than any of the others. The borosilicate glass, and glasses containing zinc, are more strongly attacked by sodium hydroxide than those containing aluminium. The glasses least attacked by water at 190° are those whose composition approaches nearest to the normal formula, $6SiO_2,R''O,R'_2O$, when R'' is calcium or zinc, but the glass least affected as regards amount of alkali dissolved, although in respect of total substance dissolved it is surpassed by Stas's calcium-potassium-sodium glass, is the Jena, 59 III, which, moreover, has the great advantage of retaining its transparency, an important point in the selection of a glass for the water-level gauges of boilers.

M. J. S.

Cementation Steel, Ferrochromium, Ferrotungsten, Chromium Steel, Tungsten Steel. By H. BEHRENS and A. R. VAN LINGE (*Rec. Trav. Chim.*, **13**, 155—181).—The specimen of cementation steel was prepared from puddled Dannemora iron; it readily fractured, and the surface was studded with glittering spangles. When polished and etched, the metal shows the presence of disseminated hard particles; these resemble white cast iron, and were isolated by dissolving the metal in acid. This substance constitutes about 5 per cent. of the steel, its hardness is slightly greater than 5; it is extremely brittle, and contains 6·6 per cent. of carbon, corresponding with the formula Fe_3C. The original steel contained 0 74 per cent. of carbon, and 0·02 per cent. of phosphorus, consequently, when freed from the carbide, it only contained 0·4 per cent. of carbon. A detailed description is given of the microscopic appearance of the steel as it gradually dissolved in acids, the portions presenting the greatest resistance to corrosion being distributed irregularly throughout the bar; this accords with Laurent's theory, that during cementation the steel derives its carbon from carbonic oxide.

Ferrotungsten, when etched, shows the presence of hard, almost rectangular, crystals. Two alloys can be distinguished, the one is white, the other grey; the hardness = 6—6·3 and 4·2—4·5 respectively. After treatment with acid, light coloured crystals separate; their hardness is between that of felspar and quartz; they are attracted by an electro-magnet, but not by a permanent one; they contain 0·56—0·62 per cent. of carbon, and probably have the formula Fe_2W. Ferrotungsten appears to resemble ferroaluminium. Attempts to isolate the compound to which tungsten steel owes its extreme hardness were unsuccessful.

Ferrochromium also contains crystals, the hardness of which = 6, whilst that of the magma = 4·2; the latter is a much better conductor of heat than the former. Treatment with acid leaves bayonet-shaped crystals, which are not magnetic; their hardness = 7·5. In ferrochromium with 13·3 per cent. of chromium, and 5·5 per cent. of carbon, the composition of these crystals corresponds with the formula $Cr_2Fe_7C_3$, corresponding with the ferrocarbide, Fe_3C; in ferrochromium with 50 per cent. of chromium, the composition is approximately Cr_3FeC_2. It is pointed out that the softer portions of the alloy contain considerable quantities of chromium, and consequently, as Hadfield has shown, the hardness is very closely connected with the quantity of carbon present; probably the action of chromium is twofold; it forms double carbides, less soluble in molten iron than the ferrocarbides, and at the same time facilitates the crystallisation of the latter. The crystals from chrome steel are smaller than those from ferrochromium, but in composition and properties closely resemble those from ferrochromium containing 13 per cent. Cr.

The paper concludes with a discussion and condemnation of the theory of the existence in various alloys of allotropic forms of the metals. Full analytical details are given, as also diagrams of some of the crystals.   J. B. T.

Chromium. By H. MOISSAN (*Compt. rend.*, **119**, 185—191).—By means of the electric furnaces previously described (Abstr., 1893,

ii, 281, and this vol., ii, 78)‚ the author has prepared more than 20 kilos. of metallic chromium.

Chromium Carbides.—When chromium is heated with a large excess of carbon in the crucible of the electric furnace with a current of 70 volts and 350 ampères for 10 or 15 minutes, the carbide, C_2Cr_3, is obtained in very brilliant lamellæ with a greasy lustre; sp. gr. = 5·62. The crystals are not attacked by concentrated or dilute nitric acid, aqua regia, or concentrated hydrochloric acid, but they are slowly decomposed by dilute hydrochloric acid. Fused potassium hydroxide has very little action on the carbide, but fused potassium nitrate attacks it readily. It is not decomposed by water even at 100°. It is much harder than quartz, and is even harder than topaz, but is softer than corundum.

Another carbide, CCr_4, is obtained in lustrous needles, sometimes 10—20 mm. long on the surface of the ingots of metallic chromium or in the cavities formed in the interior of the ingots; sp. gr. = 6·75. It is much harder than glass, and somewhat harder than quartz.

Chromium.—When the crude chromium is heated with excess of chromium oxide with a view to remove the carbon, the resulting metal is partially oxidised or " burnt." By heating the chromium in the electric furnace with calcium oxide, the greater part of the carbon is removed as calcium carbide, and the metal contains only 1·5—1·9 per cent. of carbon. When thus purified, it crystallises very readily, and the crystals, which often are 3—4 mm. long, seem to be cubes and octahedra, and resemble bismuth crystals in their grouping.

The complete removal of carbon from chromium by means of calcium oxide is not possible, because when the proportion of carbon has been reduced below a certain point, an inverse action takes place with formation of a well crystallised chromium calcium oxide. If, however, the chromium is heated in an electric furnace made of lime and brasqued with this double oxide, metallic chromium is obtained quite free from carbon; sp. gr. at 20° = 6·92.

When chromium containing 2 per cent. of carbon is heated before the oxyhydrogen blowpipe, it partially burns, with production of brilliant sparks, and the heat developed by this combustion causes the superficial fusion of the metal at the point on which the flame impinges, but the metal could not be fused in an ordinary platinum furnace even after heating for 45 minutes. Pure chromium burns in the oxyhydrogen blowpipe more brilliantly than iron, and can be completely oxidised. It is less fusible than the metal containing carbon, and its melting point is considerably higher than that of platinum, and cannot be obtained by means of the oxyhydrogen flame. In the electric furnace, however, it melts to a brilliant, very mobile liquid, and by means of a current of 70 volts and 1000 ampères, as much as 10 kilos. of chromium can be melted at once and cast into ingots.

Pure chromium is somewhat harder than glass, but not so hard as quartz; it can be worked with a file, and takes a polish similar to that of iron, but more brilliant and somewhat whiter. Chromium containing 1·5—3·0 per cent. of carbon can only be cut and polished

with a wheel armed with diamonds. The pure metal is not magnetic.

Crude chromium does not alter when exposed to moist air, but the pure metal oxidises superficially only, and afterwards undergoes no further change. It burns brilliantly in oxygen at 2000°, and burns in sulphur vapour at about 700° with formation of chromium sulphide. When heated with carbon at the temperature of a forge, it forms the carbide CCr_4, and, at the temperature of the electric furnace, the carbide C_2Cr_3. In the electric furnace, it combines readily with silicon, forming a crystallised silicide which easily scratches rubies, and is not attacked by acids, aqua regia, or fused potassium hydroxide or potassium nitrate. Under similar conditions, it forms a well crystallised boride which is very hard, and is attacked by acid with difficulty.

When heated to dull redness in hydrogen chloride, chromium is readily attacked, and yields crystallised chromous chloride. Hydrochloric acid attacks the metal very slowly in the cold, and more rapidly on heating. Under the influence of an electric current, the metal being the positive pole, it will dissolve in the dilute acid. Boiling concentrated sulphuric acid attacks chromium with evolution of sulphurous anhydride and formation of a deep coloured solution; the hot dilute acid attacks it slowly, and out of contact with air forms the blue, crystalline chromous sulphate previously described. Cold or hot fuming nitric acid or aqua regia has no action on chromium; dilute nitric acid attacks it very slowly. Mercuric chloride solution attacks the powdered metal very slowly with formation of chromic chloride.

When heated at 1200° in a current of hydrogen sulphide, chromium is completely converted into fused chromium sulphide, which has a crystalline appearance; at the same temperature, carbonic anhydride attacks the metal with formation of a superficial layer of green chromic oxide mixed with carbon, whilst carbonic oxide yields chromic oxide and carburetted chromium.

Fused potassium nitrate readily attacks chromium at a dull red heat, but the action is still more vigorous with fused potassium chlorate, on the surface of which the burning chromium floats in the same way as potassium on water. Fused potassium hydroxide, on the other hand, has no appreciable action on chromium at a dull red heat.   C. H. B.

Phosphorus Pentachloride and Molybdic Anhydride. By H. SCHIFF (*Zeit. anorg. Chem.*, **7**, 91).—A reply to Smith and Sargent (*Zeit. anorg. Chem.*, **6**, 384).

Action of Molybdenum Dioxide on Silver Salts. By E. F. SMITH and O. L. SHINN (*Zeit. anorg. Chem.*, **7**. 47—49).—The authors find that molybdenum dioxide is readily dissolved by a slightly warm aqueous solution of silver nitrate, the solution being rendered more rapid by the presence of ammonia. Silver at the same time separates out in crystalline scales.   L. T. T.

Action of Molybdic acid on Potassium Chromate and Dichromate. By R. H. BRADBURY (*Zeit. anorg. Chem.*, **7**, 43—46).—When molybdic acid is dissolved in a solution of potassium chromate, and the mixture evaporated to a small bulk, most of the acid separates unchanged; a small quantity of potassium molybdate is, however, formed, and a corresponding quantity of potassium dichromate. When molybdic acid is dissolved in potassium dichromate solution and the solution evaporated, no action appears to take place. When dry molybdic acid is mixed with dry potassium dichromate and gently fused in a crucible, a brownish powder is formed, which is insoluble in water, soluble to a green liquid in hydrochloric acid, and has the formula $K_2O,Cr_2O_3,3MoO_3$.

L. T. T.

Action of Hydrogen Chloride on Sodium Vanadate. By E. F. SMITH and J. G. HIBBS (*Zeit. anorg. Chem.*, **7**, 41—42).—Debray has shown that molybdic acid can be volatilised in a current of hydrogen chloride. The authors find that when a current of hydrogen chloride is passed over sodium vanadate, heated at 440°, the whole of the vanadic acid is volatilised, sodium chloride being left. The volatile product condensed on the cool part of the tube as a semi-opaque, reddish-brown, oily liquid, which is probably the compound $2VO_2,3H_2O,4HCl$, described by Berzelius. L. T. T.

Niobium and Tantalum. By E. F. SMITH and P. MAAS (*Zeit. anorg. Chem.*, **7**, 96—99).—Niobium oxide when heated strongly in a stream of hydrogen chloride yields a white sublimate of the formula $Nb_2O_4,3H_2O,HCl$, which the author considers to be a *hydroxychloride*. It is volatile at very high temperatures. Hydrogen bromide yields a similar *hydroxybromide*, which is yellowish-red, and rather more easily volatile than the chlorinated compound. This volatility of niobium oxide in halogen acids, although much less marked than that of molybdic acid, may give a means of removing traces of niobium from tungsten and other non-volatile substances. Tantalum oxide, under like conditions, is unchanged.

When niobium oxide is fused with a large excess of metallic magnesium, a blue-black *oxide*, Nb_2O_3, is produced. It is insoluble in all acids except hydrofluoric, and, when heated in the air, is converted into white niobium oxide. When tantalum oxide is heated with metallic magnesium, a strong action occurs, and a brownish-black *tetroxide*, Ta_2O_4, is produced; this is not attacked by hydrochloric, nitric, or sulphuric acid. When heated with chlorine, this oxide gives a white, easily volatile sublimate, which is readily decomposed by water, and contains 18·5 per cent. of chlorine. When tantalum oxide is heated with aluminium powder, violent action takes place, the whole mass becoming red hot; the above-mentioned tetroxide seems to be formed, but was never obtained free from aluminium.

L. T. T.

Haloïd Compounds of Platinum. By L. PIGEON (*Ann. Chim. Phys.*, [7], **2**, 433—502; compare Abstr., 1890, 439; 1891, 960; 1325; 1892, 3).—In addition to the tetra- and penta-hydrates of platinic chloride, the author has prepared two others. The *hepta-*

hydrate, $PtCl_4,7H_2O$, is obtained on allowing neutral platinic chloride solution to evaporate in a vacuum ; on exposure to a dry atmosphere, it effloresces, leaving the tetrahydrate. The monhydrate is formed on exposing the latter over potash in a vacuum at 100°.

Although the action of chlorine on platinum is not complete, yet on passing chlorine through arsenic chloride containing spongy platinum mixed with rather less than its weight of selenium, the whole dissolves. After heating the solution in a sealed tube at 250°, a yellow, crystalline double *compound* of platinic and selenic chlorides is deposited ; this, on heating at 360° in a current of chlorine, yields nearly pure platinic chloride. If platinum selenide is used instead of a mixture of its constituents, no action occurs. The above double compound is fairly soluble in boiling arsenic chloride, whilst platinic chloride is very sparingly so.

Platinic iodide, PtI_4, separates on adding potassic iodide to hydrogen platinochloride solution. On heating it in a current of chlorine, platinic chloride is obtained; the product nearly always contains traces of iodide.

Dry platinic iodide decomposes slowly with evolution of iodine in a vacuum at ordinary temperatures. The heat of formation of the iodide was determined.

Pt solid $+ I_4$ solid $= PtI_4$, solid, develops 17·4 Cals.

Pt solid $+ I_4$ gaseous $= PtI_4$, solid, develops 39·0 Cals.

W. J. P.

Mineralogical Chemistry.

Separation of Minerals of High Specific Gravity. By S. L. PENFIELD and D. A. KREIDER (*Amer. J. Sci.*, [3], **48**, 143—144).—The authors point out the value to mineralogists of the discovery by J. W. Retgers (Abstr., 1893, ii, 294) of the possibility of using the fused double nitrate of silver and thallium (sp. gr. = 5) for separating minerals. The liquid has the advantage of being practically colourless, neutral, soluble in water, and readily recoverable from the aqueous solution by simple evaporation on the water bath. Separations may be made in test tubes. Some disadvantages are, however, presented, and these are obviated in an apparatus, devised by the author, of which illustrations are given.   B. H. B.

Nitrogen Content of Californian Bitumen. By S. F. PECKHAM (*Amer. J. Sci.*, [3], **48**, 250—255).—The author found that the oils from the tunnels in Wheeler's Cañon on the south side of the Sulphur Mountain, Ventura Co., California, yielded the following results on analysis—

H.	C.	N.	Total.
11·82	86·93	1·11	99·86

The oil of the Pico Spring contained 1·02 per cent. of nitrogen, and that from the Cañada Laga Spring 1·08 per cent.

By washing a distillate of California petroleum with dilute sulphuric acid, basic oil is obtained, demonstrating the animal origin of the bitumens. The author has tested all of the varieties of bitumen found in California, from the most fluid petroleums to solid asphaltum, and has invariably observed the reaction indicating the presence of these compounds. B. H. B.

Natural Occurrence of Humic acid. By C. v. JOHN (*Zeit. Kryst. Min.*, **23**, 289; from *Verh. k. k. Geol. Reichsanst.*, 1891, 64).—At the outcrop of a coal seam at Theussau, near Falkenau, in Bohemia, a carbonaceous mass was met with which was completely soluble in ammonia and sodium carbonate, and was reprecipitated on the addition of hydrochloric acid. At 100° 59·25 of water was given off, the residue consisting of—

C.	H.	O.	Ash.
54·98	4·64	39·98	0·40

The formula was thus $C_{46}H_{46}O_{25}$. B. H. B.

Rumänite. By O. HELM (*Zeit. Kryst. Min.*, **23**, 308—309; from *Schriften d. naturf. Gesell. zu Danzig*, **7**, No. 4).—At several places in Roumania an amber-like fossil resin occurs, to which the author gives the name of *rumänite*. It is of a brownish-yellow · colour, transparent to translucent, much fissured, and brittle. It has a conchoidal fracture, a hardness of $2\frac{1}{2}$ to 3, and a sp. gr. of 1·048 to 1·105. Its composition is as follows.

C.	H.	O.	S.	Total.
81·64	9·65	7·56	1·15	100·00

B. H. B.

Dopplerite from Karkarala. By J. A. ANTIPOFF (*Zeit. Kryst. Min.*, **23**, 275; from *Trans. Russ. Imp. Min. Soc.*, **28**, 503—504).—This mineral gave on analysis the following results.

C.	H.	O.	S.	Ash.
55·36	6·50	34·82	0·52	2·80

Its sp. gr. is 1·13. The volatile constituents amounted to 90·20 per cent. On heating to 100°, 2·31 per cent. was volatilised. The mineral occurs in the form of a thick and extensive deposit near the Alagul salt lake. B. H. B.

Jamesonite and Plumbocuprite from Semipalatinsk. By J. A. ANTIPOFF (*Zeit. Kryst. Min.*, **23**, 275—276; from *Trans. Russ. Imp. Min. Soc.*, **28**, 527).—Analysis of jamesonite (I) and of plumbocuprite (II), from the Derwis Mine, in the province of Semipalatinsk, gave the following results.

	Cu.	Fe.	Pb.	Ag.	Sb.	S.	SiO₂.	Total.
I.	—	—	63·61	—	23·44	12·54	—	99·59
II.	69·42	0·71	9·58	0·07	trace	18·95	0·42	99·15

B. H. B.

Argyrodite and a New Sulphostannate of Silver from Bolivia. By S. L. PENFIELD (*Zeit. Kryst. Min.*, **23**, 240—248).—A specimen from La Paz, Bolivia, which was supposed to be argyrodite, gave, on analysis, the following results.

S.	Sn.	Ge.	Ag.	Zn + Fe.	Total.
16·22	6·94	1·82	74·10	0·21	99·29

In this compound, tin is, undoubtedly, isomorphous with germanium. The formula is $Ag_6(SnGe)S_6$ or $4Ag_2S,(SnGe)S_2$. The only sulphostannates hitherto known to occur in nature are the rare species *stannite*, Cu_2S,FeS,SnS_2; *frankeite*, $5PbS,Sb_2S_3,2SnS_2$; and *plumbostannite*, a mineral of doubtful composition. As the Freiberg argyrodite has been shown to be isometric, and as the name canfieldite cannot, therefore, be applied to the germanium compound, it is proposed now to transfer the name to the isomorphous tin compound.

B. H. B.

Identity of Hydrofranklinite and Chalcophanite. By S. L. PENFIELD and D. A. KREIDER (*Amer. J. Sci.*, [3], **48**, 141—143).—The name of hydrofranklinite was given by W. T. Roepper to a supposed new hydrous oxide of iron, zinc, and manganese from Stirling Hill, New Jersey. The original chemical examination was never completed, and a new analysis has given the following results.

FeO.	ZnO.	MnO.	O.	H_2O.	Insol.	Total.
10·00	18·25	48·27	11·21	11·85	0·25	99·83

The composition of the mineral can be expressed by the formula $RMn_2O_5,2H_2O$, a formula identical with that derived by Moore in 1875 for chalcophanite.

B. H. B.

Leadhillite in Missouri. By L. V. PIRSSON and H. L. WELLS (*Amer. J. Sci.*, [3], **48**, 219—226).—The rare hydrated sulphato-carbonate of lead has been reported from but three localities in the United States. A new occurrence is now announced, near Granby, Missouri. The crystals are hexagonal prisms terminated by the base, the colour varying from colourless to clear sea-green. Analysis yielded the following results.

SO_3.	CO_2.	PbO.	H_2O.	Total.
7·33	8·14	82·44	1·68	99·59

The formula is thus $PbSO_4,2PbCO_3,Pb(OH)_2$, corresponding with the composition suggested by Groth.

B. H. B.

Alunite from Colorado. By E. B. HURLBURT (*Amer. J. Sci.*, [3], **48**, 130—131).—The alunite described occurs as an aggregate of minute crystals filling pockets in the ore-body of the National Belle Mine, Red Mountain, Ouray Co., Colorado. On analysis, the mineral yielded

SO_3.	Al_2O_3.	K_2O.	Na_2O.	H_2O.	Insol.	Total.
38·93	39·03	4·26	4·41	13·35	0·50	100·48

The results agree satisfactorily with the commonly accepted formula $KAl_3S_2O_{11},3H_2O$. An interesting feature is, however, the large percentage of soda, alunite having usually been regarded as a potash compound only. Another interesting feature is the insolubility of the mineral in hydrochloric acid. B. H. B.

Magnetostibian, a New Antimony Mineral. By L. J. IGELSTRÖM (*Zeit. Kryst. Min.*, **23**, 212—214).—In appearance, this mineral, which was found at the Sjö mine, resembles magnetite and jacobsite. It differs, however, from them in being transparent with blood-red colour under the microscope. It occurs in the form of grains in limestone. After the impurities had been removed, the magnetostibian gave, on analysis, the following results.

Sb_2O_3.	As_2O_5.	FeO.	MnO.	Fe_2O_3.
9·83	1·54	17·16	59·11	12·36

The formula may be expressed thus $(MnO,FeO)_{35},Sb_2O_5$. The name of magnetostibian has been selected for this mineral to indicate its magnetic properties, its similarity to magnetite and its percentage of antimony. B. H. B.

Humite free from Fluorine. By P. JANNASCH and J. LOCKE (*Zeit. anorg. Chem.*, **7**, 92—95).—Schäfer found in serpentine from the Allalinhorn, Switzerland, two minerals, one brownish-yellow and monoclinic, the other colourless, which from their optical characters are evidently humites. Both were free from fluorine. The brown mineral gave analytical results agreeing with the formula

$$Mg_5(Mg \cdot OH)_2(SiO_4)_3.$$

The colourless mineral could not be obtained quite free from impurity, but appears to have the formula $Mg_7(Mg \cdot OH)_2Si_3O_{15}$. L. T. T.

Constitution of the Zeolites. By F. W. CLARKE (*Amer. J. Sci.*, [3], **48**, 187—193).—The obvious relationship of many zeolites to the felspars has long been recognised as a probable key to their constitution, but hitherto no systematic theory of the connection between the two groups has been put forward. This has now been developed by the author, and a preliminary statement of the conclusions reached is given. The complex aluminous silicates are regarded as generally being substitution derivatives of simple normal salts, and the acid radicles SiO_4 and Si_3O_8 are regarded as being mutually replaceable. From the albite and anorthite formulæ given by the author, those of many zeolites are easily derived, providing that the assumption is made that the soda salt may be replaced by its equivalent ortho-compound, and the calcium salt by the corresponding trisilicate. All water in the zeolites being regarded as water of crystallisation, and the groups SiO_4 and Si_3O_8 being represented by the general symbol X, the greater number of the numerals under consideration easily fall into two groups, having the following generalised formula.

I. $Al_6X_6R_6'$, nAq, and $Al_3X_3R_3'$, nAq.
II. $Al_4X_6R_{12}'$, nAq, and $Al_2X_3R_6'$, nAq.

The two groups remain in this form, however, only so long as water is ignored; for when the latter is regarded as partly constitutional, several members of the first series must be transferred to the second.　　　　　　　　　　　　　　　　　　　　　　　　B. H. B.

Microcline and Hornblende from Durbach. By A. SAUER (*Zeit. Kryst. Min.*, **23**, 291; from *Mittheil. Grossh. bad. Geol. Lande-,sanst.*, **2**, 233).—In the normal granitite of Durbach, in the north of the Black Forest, small crystals of microcline (I) occur, containing a little albite. From the Durbach mica-syenite, pure material of blackish-green hornblende (II), of sp. gr. 2·94 to 2·96 was isolated by ,means of Klein's solution. The analytical results were as follows.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	64·53	19·14	trace	—	0·44	—	12·40	2·89	0·34	99·74
II.	54·89	1·50	5·06	7·46	12·08	16·01	0·38	0·37	2·72	100·47

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Analyses of Hornblende. By A. BRUNLECHNER (*Zeit. Kryst. Min.*, **23**, 292—293).—Analyses of hornblende from hornblende-eclogite from Semlach (I), from Lölling (II), and from Wölch (III), in ·Carinthia, gave the following results.

	SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	Total.
I.	48·80	14·45	16·77	1·14	11·26	0·43	92·85
II.	45·66	14·88	17·44	1·44	10·27	4·52	94·21
III.	47·02	11·79	17·20	0·70	14·56	0·77	92·04

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Bauxite from the Vogelsberg. By A. LIEBRICH (*Zeit. Kryst. Min.*, **23**, 296).—Bauxite occurs in large quantities at the Vogelsberg as an alteration product of plagioclase-basalt. The author gives ·the following analyses ,of bauxite :—I, a crystalline variety from ·Grabenteich; II, an amorphous variety from the Schäferling mine ,near Lich ; and III, an amorphous variety from the Firnewald mine.

	SiO_2.	Al_2O_3.	Fe_2O_3.	TiO_2.	CaO.	MgO.	H_2O.	Total.
I.	1·10	50·92	15·70	3·20	0·80	0·16	28·60	100·48
II.	2·78	50·52	13·09	3·08	1·66	trace	27·12	99·15
III.	4·92	53·10	10·62	2·80	0·62	trace	27·80	99·86

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Sericite from Tetschen. By E. HIBSCH (*Zeit. Kryst. Min.*, **23**, 290; from *Jahrb. k. k. Geol. Reichsanst.*, **41**, 235).—Sericite (sp. gr. 2·88), from the sericite-gneiss on the right bank of the Elbe, near Tetschen, isolated by means of potassium mercury iodide solution, gave, on analysis, the following results.

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
47·97	35·95	3·13	0·55	0·25	8·58	0·54	4·53	101·50

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Analysis of Garnet. By W. MÜLLER (*Zeit. Kryst. Min.*, **23**, .292 ; from *Zeit. Deutsch. Geol. Ges.*, **43**, 730).—Garnet crystals, of a blood-red colour, from the contact-metamorphosed mica-schist of the Schneekoppe, were found to have the following composition.

SiO$_2$.	Al$_2$O$_3$.	Fe$_2$O$_3$.	FeO.	MnO.	CaO.
34·54	22·26	7·09	32·74	2·32	1·33

B. H. B.

Rocks and Minerals from the Island of Rhodes. By H. v. FOULLON (*Zeit. Kryst. Min.*, **23**, 293—294; from *Sitzungber. k. k. Akad. Wiss. Wien.*, **100**, 144).—The author gives descriptions and analyses of felspar from the uralite gabbro of Rhoino, and from the *flysch* of Sklipio. To the same geological horizon belong asbestos-like schists, of which three varieties are described. In conclusion, he describes an asbestos-like variety of glaucophane, in which the greater portion of the Al$_2$Si$_3$O$_9$ is replaced by Fe$_2$Si$_3$O$_9$. For this, he proposes the name of *rhodusite*. B. H. B.

Nepheline-syenite of Dungannon, Ontario. By B. J. HARRINGTON (*Amer. J. Sci.*, [3], **48**, 16—18).—A remarkable mass of nepheline-syenite has been discovered at Dungannon, Hastings Co., Ontario. The rock is coarse in texture, and individuals of nepheline (Analysis I), as much as $2\frac{1}{2}$ feet in diameter, have been observed. Sodalite (Analysis II) was found in the form of veins, streaks, and irregular masses in the rock, and the sodalite is, in places, traversed by little veins of a white and reddish mineral, which proves to be orthoclase (Analysis III). The felspar of the nepheline syenite being entirely plagioclase, the occurrence of orthoclase as a scondary mineral in the sodalite is of special interest. The following are the analytical results.

	SiO$_2$.	Al$_2$O$_3$.	Fe$_2$O$_3$.	FeO.	CaO.	MgO.	K$_2$O.	Na$_2$O.
I.	43·51	33·78	0·15	—	0·16	trace	5·40	16·94
II.	36·58	31·05	—	0·20	—	--	0·79	24·81
III.	63·00	18·93	0·59	—	0·08	0·09	12·08	3·67

	H$_2$O.	SO$_3$.	Cl.	Insol.	Loss on ignition.
I.	—	—	—	—	0·40
II.	0·27	0·12	6·88	0·80	—
III.	—	—	—	—	1·00

B. H. B.

Physiological Chemistry.

Respiratory Exchange in Cold Blooded Animals. By H. M. VERNON (*J. Physiol.*, **17**, 277—292).—Observations made on frogs by the use of the Pembrey-Haldane apparatus, showed :—

The evolution of carbonic anhydride in intact frogs, on gradual warming, varies within narrow limits from 2° up to 17·5°, but above this point it increases rapidly with the temperature. On cooling, it,.

as a rule, becomes nearly constant from about 17·5° to 12·5° or 10°, and then decreases uniformly with the temperature.

In curarised frogs, and frogs with their bulb injured, the discharge of carbonic anhydride increases uniformly with the temperature.

If frogs are warmed and cooled rapidly several times, the curves of carbonic anhydride evolution subsequently obtained are either perfectly uniform or show abnormally marked changes at varying temperatures. The curves do not become normal again for several days after.

The respiratory quotient of winter frogs in which the bulb has not been injured is about 0·63 ; that of frogs with the bulb injured about 0·45 ; and that of curarised frogs, and frogs subjected to rapid temperature changes about 0·5.　　　　　　　　　　　　　W. D. H.

The Action of Different Acids on Gastric Digestion. By M. HAHN (*Virchow's Archiv*, **137**, 597—604).—Various forms of proteïd were digested with the usual mixture of pepsin and hydrochloric acid. In other experiments, equivalent quantities of other acids, organic and inorganic, were substituted for the hydrochloric acid. Hydrochloric acid is the most efficient acid, then comes nitric, sulphuric, and phosphoric acids in the order named, if the albumin is in solution. If, however, fibrin is used, phosphoric acid is better than sulphuric ; and, for several reasons, phosphoric acid is recommended as the best substitute for hydrochloric acid. The organic acids have much less power ; tartaric, oxalic, and citric acids appear to be the best ; acetic acid is very feeble. Boric acid has no action at all.

W. D. H.

Proteolysis of Crystallised Globulin. By R. H. CHITTENDEN and L. B. MENDEL (*J. Physiol.*, **17**, 48—80).—This is an account of a renewed examination of the products of the action of pepsin hydrochloric acid. The proteïd selected was crystallised globulin or vitellin from hemp seed. The paper gives an account of two digestions, one of which was continued for three, and the other for ten days. The products of the digestion were carefully separated from one another and analysed ; their reactions are exhaustively described, including their specific rotatory power. In separating proteoses from peptone, the difficulties of manipulation are recognised, and, so far as is at present possible, obviated. The investigation lends, however, no support to Pekelharing's suggestion that peptone is merely a portion of unprecipitated proteose ; whilst it is in accordance with Kühne's view that it is a definite, well-characterised substance. Its amount increases, and that of proteose diminishes, as digestion progresses, but a digestion in which all proteose has been converted into peptone has not yet been obtained. The progressive changes from primary proteose to deutero-proteose and peptone are most prominent in the early stages of digestion ; the disappearance of deutero-proteose and the formation of peptone is subsequently a very gradual process.

In the proteolytic process, at least four products of hydration and cleavage are easily recognisable, namely, proto-proteose, hetero-proteose, deutero-proteose, and peptone. The examination of the

percentage composition of these substances shows a gradual and progressive falling off of carbon as digestion progresses. But the tables given show another very noticeable feature, and that is that the percentage composition of the individual proteoses differs in the two digestions; the substance called proto-vitellose, for instance, in the digestion carried on for three days, cannot be the same as that with the same name in the digestion carried on for the ten days, although both give the same reactions, specific rotation alone excepted. The authors protest that this cannot be due to analytical errors, and state that other proteïds, egg albumin, for instance, give similar results. The explanation advanced is that the four substances named merely represent the main steps in the hydration process, but that there are further links in the chain mixed with these which cannot at present be separated, and which manifest the same general chemical behaviour.   W. D. H.

Nutritive Value of Sugar. By N. Zuntz (*Chem. Centr.*, 1894, i, 691—692; from *Zeit. Ver. Rubenzuck.*, 1894, 64—71).—By causing a dog to mount continuously a plane inclined at 10° to the horizon, and analysing the expired air, it is possible to calculate the amount of oxygen used per kilogram-metre of work done, and also the quantity of heat produced by the combustion in which this oxygen took part. The amount of oxygen used per kilogram-metre of work done was found to be, for a diet of *lean meat*, 0·57 c.c. (2 58 Cal.); *fat*, 0·53 c.c. (2·43 Cal.); *cane sugar*, 0·54 c.c. (2·58 Cal.). Sugar, fat, and lean meat have thus about the same power of enabling physical exertion to be sustained. The efficiency of the animal body, considered as a machine, was found to be about one-third, whereas with steam-engines only one-twentieth to one-fifth of the energy of the fuel is obtained as mechanical work.   C. F. B.

Presence of Hydrogen and Methane in the Residual Nitrogen from Blood. By L. DE SAINT MARTIN (*Compt. rend.*, 119, 83—85).— The residual nitrogen from the blood of an ox was found to contain hydrogen amounting to 0·41—0·64 c.c., and methane amounting to 0·68—0·69 c.c. per 1,000 c.c. of defibrinated blood.   C. H. B.

Nucleo-albumins and Intravascular Coagulation. By W. D. HALLIBURTON and T. G. BRODIE (*J. Physiol.*, 17, 135—173).—A large number of experiments on rabbits are recorded, and the general properties of nucleo-albumins prepared from numerous tissues and organs are given. The general conclusions drawn are the following :—

1. There are two methods of preparing nucleo-albumin from organs : (1) Wooldridge's acetic acid method, and (2) a new method, consisting in the alternate treatment of the finely-minced organ or tissue with sodium chloride and water, for details of which the reader is referred to the original paper.

2. The material obtained by both methods from the same organ is the same in (1) general proteïd reactions, which closely resemble those of the globulins; (2) percentage of phosphorus; and (3) physiological action, that is, the production of intravascular coagula-

tion; death is due to cessation of respiration, primarily caused, probably, in the respiratory centre.

3. The nucleo-albumins obtainable from various organs differ in some minor points, the most important being the amount of nuclein (as evidenced by phosphorus estimation) in combination with the proteïd.

4. The sodium carbonate used as a solvent for these substances does not produce thrombosis.

5. Protagon, the most abundant impurity in these preparations, is also not responsible for the intravascular clotting.

6. These nucleo-albumins do not accelerate the coagulation of extravascular (dilute salted) plasma, and so contrast very forcibly with fibrin-ferment. The differences between fibrin-ferment and nucleo-albumin are so striking that they are possibly different substances, each, however, capable of producing fibrin under appropriate conditions.

7. Experiments with "peptone" and leech extract confirm the hypothesis of Pekelharing that these substances hinder coagulation on account of their affinity for calcium.

8. Rabbits do not show Wooldridge's "negative phase" of coagulation, but the experiments recorded, together with those of C. J. Martin (this vol., ii, 58), lend no support to the theory of Wright and Lilienfeld that this "negative phase" is produced by the splitting off of a peptone-like substance from the nucleo-albumin.

9. Typical intravascular coagulation did not, however, always occur, and the principal sources of failure are four in number.

10. The first of these relates to idiosyncrasies in the rabbit tribe, albinos being very resistant to the action of nucleo-albumin.

11. The second is due to the keeping of the nucleo-albumin too long either in contact with the acid or with the alkali carbonate used in its preparation.

12. The third is the too rapid preparation of the material. A fresh thymus yields to sodium carbonate a nucleo-albumin which is inactive, and probably is a zymogen of the active substance. A thymus which has been allowed to decompose slightly, or in which its cellular structure has been thoroughly destroyed by grinding up with sand, if treated for a few hours with dilute acetic acid yields nucleo-albumin active in producing thrombosis.

13. The fourth is due to attempts to purify the material too thoroughly. Frequent alternate treatment with acetic acid and sodium carbonate, or with sodium chloride and water, produces not only a substance which is inactive physiologically, but also one which is chemically different from the original. The chemical change is not the same in the two cases. Repetition of the sodium chloride method of preparation causes a fall in the percentage of phosphorus, due to removal of nuclein, and a rise in the amount of ash, of which, however, sodium chloride itself forms a constant but insignificant fraction. Repetition of the acetic acid method causes either no change in the proportion of phosphorus, or more frequently a rise due to removal of the proteïd constituent of the nucleo-albumin. These statements are illustrated by tables of analyses.

14. Solutions of nucleo-albumin destroy the blood corpuscles, especially the multinucleated white ones ; this, however, is largely due to their alkalinity, and will not explain the thrombosis produced. Other leucolytic agents will not produce thrombosis, even when calcium chloride is injected as well, and the experiments performed in this direction have entirely failed to confirm Löwit's work on this question.

W. D. H.

Proteïds of Red Marrow. By J. R. FORREST (*J. Physiol.*, **17,** 174—176).—In the thymus and lymphatic glands are large collections of non-eosinophile cells, and these yield nucleo-albumin active in producing thrombosis (see preceding abstract). In the red marrow is a collection of cells which are mostly eosinophile, the granules of which give microchemically the reaction for phosphorus introduced by Lilienfeld and Monti (Sherrington, *Proc. Roy. Soc.*, **55**, 161). It was judged necessary to investigate the proteïds of red marrow macrochemically. The results obtained did not show any difference from those obtained from the thymus. The principal proteïd obtained is nucleo-albumin, which can be prepared by both methods (see preceding abstract). It causes intravascular clotting, and is preceded in the cells by something resembling a zymogen. In addition to this, there is a globulin coagulated by heating at 47—50°, traces of an albumin and of hæmoglobin, but proteose and peptone are absent. The estimation of phosphorus in the nucleo-albumin was not performed.

W. D. H.

Oxalates and Muscle Rigor. By F. S. LOCKE (*J. Physiol.*, **17,** 293—295).—The exposure of frog's muscle to solutions of sodium oxalate does not prevent the occurrence of *rigor mortis*, nor altogether abolish the irritability of the tissue. From this, the conclusion is drawn, not that calcium is unnecessary in these processes, but rather that it is held by the tissue so firmly that oxalate does not remove it.

W. D. H.

The Vitreous and Aqueous Humors. By W. PAUTZ (*Zeit. Biol.*, **31,** 212—243).—The paper relates specially to the question whether the aqueous and vitreous humors of the eye contain urea, dextrose, and sarcolactic acid or not. Urea was found in the vitreous humor (0·051 per cent.) and in the aqueous humor of the ox. Dextrose was found in both humors. The possibility that aqueous humor contains another reducing substance in addition was not investigated. The vitreous humor contains sarcolactic acid, or, more probably, salts of the acid. The aqueous humor contains the same substance, but the quantity obtained was too small to admit of a complete analysis.

W. D. H.

Succinic acid. By F. BLUMENTHAL (*Virchow's Archiv*, **137,** 539—568).—The best method for the isolation of succinic acid is its extraction by means of ether containing alcohol. The purification of the product obtained by evaporating the solvent, varies under certain circumstances, treated at length in the paper. Admixtures due to putrefaction can be obviated by fractional acidifying the extracting reagent.

Succinic acid is a product of the vital activity of different micro-organisms, and can be formed by these from carbohydrates, from substances allied to carbohydrates, and from albumin. Its quantity in the last-named case is dependent on the alkalinity of the mixture.

The organs obtained in the physiologically fresh condition contain no succinic acid. When it is found in them, it is a *post-mortem* product. It is, therefore, not a metabolic product of animal cells, but of micro-organisms.

Milk, on standing for months in an acid condition, contains the acid. Bacteriological investigation of such milk reveals the presence of (among others) short, rod-like microbes, which liquefy gelatin, forming there round, sharply-limited colonies. Infection of other milk with a culture of these, leads, in a few days, to the formation of succinic acid.   W. D. H.

Formation of Sulphuric acid in the Organism. By E. Salkowski (*Virchow's Archiv*, **137**, 381—384).—Polemical. It is pointed out that E. Baumann, in making abstracts of the papers of the author and his assistants, has misunderstood or misinterpreted his views on the subject.   W. D. H.

Bile Pigments. By A. Jolles (*Pflüger's Archiv*, **57**, 1—57).— Pure bilirubin is, in time, completely converted into biliverdin by the use of a dilute solution of iodine in alcohol (N/100). A similar oxidation occurs more rapidly by using Hübl's iodine solution of the same strength. The reaction may be denoted by the equation:

$$C_{32}H_{36}N_4O_6 + 4I + 2H_2O = C_{32}H_{36}N_4O_8 + 4HI.$$
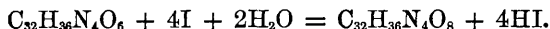
This fact may be utilised for the estimation of bilirubin titrimetrically. The requisites are (1) centinormal iodine solution in alcohol, (2) centinormal solution of sodium thiosulphate, and (3) freshly-prepared starch solution. The end reaction, namely, the characteristic colour and spectrum of biliverdin, is not seen until the bilirubin is completely changed into biliverdin. The characteristic spectrum of bilirubin is a dark band between D and E ($\lambda 8\cdot8$ to $9\cdot1$), and a complete absorption of light beyond $\lambda 4\cdot9$ and 11 in each direction. Biliverdin shows two bands, one before the D line, the other after ($\lambda 7\cdot1$ to $8\cdot1$, and $8\cdot9$ to $9\cdot1$), and a complete absorption of light beyond $6\cdot4$ and 14 in each direction. 1 c.c. of centinormal iodine solution $= 0\cdot00127$ gram iodine $= 0\cdot00144$ gram bilirubin.

The percentage of bilirubin in ox-bile varies from $0\cdot024$ to $0\cdot027$. The quantity of biliverdin is very much less, in spite of the green colour of the fresh bile. The specimens examined were found to be slightly acid. Saponifiable substances were only present in minimal quantities. Pig's bile contains from $0\cdot051$ to $0\cdot206$ per cent. of bilirubin. It is richer in urobilin and is more viscid than ox-bile. It also contains a red pigment of uncertain nature, soluble in acid amylic alcohol. It is slightly acid, rather more so than ox-bile. Saponifiable substances are absolutely small in amount, but relatively thrice as abundant as in ox-bile. Dog's bile and human bile are also slightly acid. Human bile contains $0\cdot154$ to $0\cdot262$ per cent. of bilirubin.

The acidity and amount of saponifiable substance were greater in the specimens of human bile examined than in those of the lower animals.

W. D. H.

Glycerophosphoric acid. By K. Bülow (*Pflüger's Archiv*, **57**, 89—92).—The amount of glycerophosphoric acid was determined in a dog's urine by first precipitating the phosphates, then evaporating the filtrate nearly to dryness with hydrochloric acid; the phosphate so formed was then estimated. The amount averaged 0·00619 per diem. It was very slightly increased by the administration of glycerophosphates, either by the mouth or subcutaneously, and not at all increased by salol. It thus appears that the glycerophosphoric acid obtained from the lecithin of the food, or given as such, is, in great measure, destroyed in the organism; only traces pass out unchanged. The experiments with salol show that phosphoric acid does not, like sulphuric acid, form ethereal hydrogen salts with phenol-like substances.

W. D. H.

Physiological Action of certain Derivatives of Benzaldehyde. By K. Bülow (*Pflüger's Archiv*, **57**, 93—96).—The four substances investigated— hydrobenzamide, benzylidenediformamide, benzylidenediacetamide, and benzylidenediureïde—agree in that they are all easily broken up into their components by dilute cold mineral acids.

Hydrobenzamide led, in dogs and rabbits, to the appearance of hippuric acid in the urine. There were also symptoms of acid poisoning, which, in rabbits, proved fatal.

Benzylidenediacetamide was given to a dog. The greater part appeared as such in the urine. Hippuric acid was not present, and ethereal hydrogen sulphates were not increased.

Benzylidenediformamide is more easily decomposed than the preceding drug, both within and without the body. The decomposition that occurs within the body is not, however, very great, there only being in the urine a small amount of hippuric acid. Ethereal hydrogen sulphates were unchanged.

Benzylidenediureïde was easily split in the body into urea and benzaldehyde, the latter passing out in the urine as hippuric acid.

Other benzaldehyde-derivatives (amarin, methylamarin, lophin) were investigated. The two first produced loss of appetite and sickness, and amarin produced convulsions also. Lophin had no such action. No details are given of the urine.

W. D. H.

Physiological Action of Pyridine. By T. L. Brunton and F. W. Tunnicliffe (*J. Physiol.*, **17**, 272—276).—From experiments on frogs, guinea-pigs, and rabbits, the following conclusions are drawn.

1. Pyridine is not, as compared with its derivatives, an active poison ; it would hardly be expected to be so, *à priori*, as it is an exceedingly stable substance.

2. Its action is almost confined to the sensory part of the nervous system. In small doses it has a stimulating, in large doses a direct paralysing action on the cardiac muscle.

W. D. H.

Piperazine. By BIESENTHAL (*Virchow's Archiv*, **137**, 51—77).—
Piperazine is here extolled as a drug in gout and allied manifestations
of the uric acid diathesis. It is stated to possess a powerful solvent
action on uric acid deposits and calculi.   W. D. H.

Phloridzin Diabetes. By P. A. LEVENE (*J. Physiol.*, **17**, 259—
271).—Some observers think that phloridzin glycosuria is the result
of a simple elimination of sugar from the organism by the kidneys ;
others see in it an excessive formation of glucose. The first base
their view on the slight decrease of sugar in the blood after the
injection of the drug, and on the fact that after the extirpation of the
kidneys the quantity of sugar in the blood is somewhat increased in
some cases. But no one has succeeded in establishing a fixed relation
between the quantity of sugar in the blood and the sugar eliminated.
In the present research on dogs, a decrease of sugar in the blood was
noted in some experiments when the phloridzin was injected after
ligation of the renal vessel. Cornevin (*Compt. rend.*, **116,** 263) showed
that phloridzin greatly increases the quantity of sugar eliminated by
the milk.   Consequently the poison does not affect the kidneys only.
The operation of extirpation of the kidneys is not considered decisive
of the question of the origin of the glycosuria.

As to the second view, that there is an increased production of
sugar, and that, more especially, by the kidneys, it is found that the
venous blood of the kidneys in phloridzin glycosuria contains, in
some cases, more sugar than the arterial, and that the quantity of
sugar in the kidney tissue itself increases after the injection of
phloridzin.

Finally, the composition of the blood in phloridzin diabetes testifies
to the decomposition of proteïds rather than to a mere elimination of
sugar.   W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Chlorides on Nitrification. By J. CROCHETELLI and J. DUMONT (*Compt. rend.*, **119**, 93—96).—When potassium chloride is added to a soil containing calcium carbonate, the drainage water contains calcium chloride. Direct experiments show that the latter salt has a distinctly retarding influence on nitrification. If, however, the soil is washed with a small quantity of water, the retarding effect disappears, and soil which has been mixed with potassium chloride and then washed shows a marked increase in nitrification. This fact explains the different effects produced on crops by alkali chlorides in dry seasons and in rainy seasons. Large proportions of potassium chloride, however, retard nitrification under any conditions.

Sodium chloride behaves similarly, probably because in soils rich in potassium compounds it is first more or less completely converted into potassium chloride.

The efficiency of potassium chloride in promoting nitrification is

due entirely to its conversion into potassium carbonate by contact with calcium carbonate, for it produces no effect on soils that do not contain calcium carbonate. C. H. B.

Composition of Honey Dew, and its Influence on the Constitution of Honey.

By E. v. RAUMER (*Zeit. anal. Chem.*, **35**, 397—408).—Honey dew is a viscid, saccharine substance found on the leaves of various plants, especially in warm, dry summers. It is partly an exudation from the leaves themselves, and is partly excreted by aphides. It is collected by bees as one of the materials for their honey. It was unusually copious in 1893, and the author collected a large specimen by rinsing the leaves of the maple with cold water. Samples of honey of the same season were also examined. The analysis of the honey dew showed much cane sugar, a little inverted sugar, and much unfermentable dextrin, together with ash and nitrogenous substances. A specimen of the dextrin was prepared from the residues of the fermentation, and found to have a specific rotatory power $[\alpha]_D^{20°} = 181·5$, to be almost free from reducing action on Fehling's solution, and to be very slowly diffusible. In addition, there was obtained evidence of a substance, seemingly of the dextrin class, which furnished alcohol on fermentation, but was incapable of reducing copper solution. The honey samples showed abnormally large amounts of fermentable and non-fermentable, dextro-rotatory, but not copper-reducing, constituents (dextrins), the latter of which was, however, much more diffusible than that of honey dew. The author attributes the presence of these substances to contamination with honey dew, and suggests that the superior diffusibility of the dextrin in honey is due to some change which has occurred in the honey gland of the bee. On this ground, he concurs in the proposal of Haenle (this vol., ii, 164), to examine honey by dialysis, but advises that the fermented honey should be employed, since the sugars of unfermented honey dialyse out very slowly. The presence of this hitherto overlooked fermentable dextrin in genuine honey accounts for the fact that all analyses show a deficiency. The amount fermented depends, however, on the kind of yeast used.

M. J. S.

Composition of the Seeds and Etiolated Sprouts of Hemp (Cannabis sativa) and Sunflower (Helianthus annuus).

By S. FRANKFURT (*Landw. Versuchs-Stat.*, **45**, 153—154; compare this vol., ii, 113).—A further examination of hemp seeds showed that they contain, besides choline, a second base, identical with E. Jahn's trigonelline, $C_7H_7NO_2$ (Abstr., 1886, 85, and 1888, 166), obtained from *Trigonella foenum graecum*. The author has also obtained this base from peas. N. H. M.

Substances occurring with the Waxy Matters of some Fruits and their Skins.

By W. SEIFERT (*Landw. Versuchs-Stat.*, **45**, 29—35; compare this vol., i, 256).—The fruits examined were apples, pears, plums, bilberries, and sloes. The substances were extracted with chloroform, and the residue obtained, after distilling off the chloroform, extracted with light petroleum in a Soxhlet apparatus.

The undissolved portion was then crystallised from alcohol. The waxy matter dissolved in the light petroleum was freed from chlorophyll by extracting it with alcohol.

Apple peel yielded a quantity of waxy matter and a good deal of a substance resembling vitin in many respects. It forms a yellowish-white, amorphous powder, which when heated becomes brown and melts at 234°. It could not be crystallised from alcohol, is insoluble in water, nearly insoluble in light petroleum, but rather readily soluble in alcohol, ether, and chloroform. Its solution in strong sulphuric acid is orange-red. With acetic anhydride and a few drops of sulphuric acid, it gives a reddish-violet coloration, which becomes cherry coloured on adding more acid. The waxy substance is nearly white, melts at 64°, and when heated has an intense odour, resembling that of amyl alcohol.

Pear skin gave a wax melting at 68°, and an amorphous substance melting at 240°; the latter resembles the compound obtained from apples in solubility, gives a brownish-yellow solution in sulphuric acid, and an intense purple coloration with acetic anhydride and sulphuric acid. The solution becomes slightly fluorescent when much acid is added.

Bilberries gave a wax melting at 71°, and a crystalline compound, probably vitin. It forms white, concentrically grouped needles with a silky lustre, melting at 255—260° after darkening. The specific rotation $[\alpha]_D = +60.72°$. It resembles vitin in its behaviour towards sulphuric acid, and towards acetic anhydride and sulphuric acid. The calcium and copper salts were prepared and analysed.

Ripe plums yielded a small quantity of a substance resembling vitin, and a wax melting at 64°.

Fresh, ripe sloes yielded a wax melting at 67.5°, and an amorphous substance which melted at 228—230°, and gave similar colour reactions to the compounds already described. The alcoholic solution when treated with potash or ammonia showed an intense blue fluorescence, due to the presence of a second compound which could be dissolved out with hot water.

Tables are given showing the absorption spectra of the solutions of the compounds.   N. H. M.

Can Non-Leguminous Plants fix Free Nitrogen? By F. NOBBE and L. HILTNER (*Landw. Versuchs-Stat.*, **45**, 155—159).—After it was established that Leguminosæ, when suitably infected with nodule bacteria, have the power of assimilating free nitrogen, the authors showed that under similar conditions the same holds good with Elæagnus, and with the white and black alder. Podocarpus, a conifer, which also has root nodules, seems likewise to have the power of fixing nitrogen. The same property has recently been frequently attributed also to non-leguminous plants, which have no root nodules, the evidence being that the final nitrogen in the plants and soil was greater than the initial nitrogen in the seeds and soil.

In the first experiments now described, mustard was grown in sand and supplied with different amounts of nitrogen. Like leguminous plants when free from nodules, the growth of mustard depended

entirely on the amount of nitrate given, and there was no assimilation of free nitrogen.

Peas, mustard, buckwheat, and oats were next grown in a mixture of sand and garden soil. The mixture was first sterilised, and then seeded with an extract of pea, mustard, buckwheat, and oat soils. Seeds were sown three times. In the case of the first crops, all the plants grew well; in the second, there was a marked falling off in the case of the non-leguminous plants, which soon showed nitrogen hunger.

The following table includes all three crops.

	Nitrogen (grams).				
	Initial.		Final.		
	In soil.	In seeds.	In soil.	In produce.	Gain.
Peas.............	3·320	0·401	3·399	0·859	0·537
Mustard	3·320	0·018	3·269	0·305	0·236
Buckwheat........	3·320	0·027	3·326	0·276	0·255
Oats	3·320	0·048	3·618	0·487	0·737
Fallow...........	3·320	—	3·374	—	0·054

There was thus a gain in every case, even more with oats than with peas. The slight gain in the fallow plot is within the error of experiment. The following conclusions are drawn from these results.

The pea alone collects nitrogen for its own use, the three other plants, notwithstanding the increase of nitrogen in the soil, did not thrive. Peas, and doubtless all nodule bearing plants, occupy an isolated position as regards nitrogen fixation, and do not differ from other plants merely in degree. The non-leguminous plants did not themselves fix the nitrogen by which the soil was enriched; the fixation must have taken place in the soil itself, probably as the experiments of Winogradsky, Berthelot, and others indicate, by means of soil bacteria. The nitrogen so fixed does not seem to be immediately available for plants, and probably has first to be nitrified.

N. H. M.

Analytical Chemistry.

Applications of the Gas Baroscope. By G. BODLÄNDER (*Zeit. angw. Chem.*, 1894, 425—431).—The author recommends the use of his gas baroscope (this vol., ii, 440) in the analysis of commercial products. Carbonates are decomposed by excess of acid; bleaching powder, pyrolusite, and potassium permanganate are decomposed by means of

hydrogen peroxide. Carbon in iron is estimated by heating the sample with sulphuric and chromic acids, without previous separation of the carbon, in an Ullgrén's apparatus, which is directly connected with the baroscope. Oxalic acid or oxalates are best treated with a mixture of dilute sulphuric acid and potassium permanganate. Manganese may be estimated in steel by first treating the sample with nitric acid and potassium chlorate, and finally treating the manganic dioxide with sulphuric acid and oxalic acid. Potassium permanganate may in turn also be checked by means of sulphuric acid and oxalic acid.

L. DE K.

A Simple Apparatus for Measuring Gases. By C. KIPPEN-BERGER (*Zeit. angw. Chem.*, 1894, 517—520).—The apparatus consists of a cylinder, A, provided with a calibrated scale divided to 0·1 cm. Inside are placed two bent tubes, a and b, which are so constructed that they both have the same capacity, and that when the apparatus is filled the meniscus of the liquid in each is in the same line with that in the stop-cock, 2. B is a cylinder calibrated to 0·1 c.c., and C a similar one, though somewhat narrower, and consequently holding less liquid, and also having an inside tube calibrated to 0·1 c.c., and closed by means of an india-rubber tube. The apparatus is filled by connecting the tube b with a Woulff's bottle by means of an india-rubber tube. The Woulff's bottle is filled with any suitable liquid, which is forced out by means of the rubber force-pump.
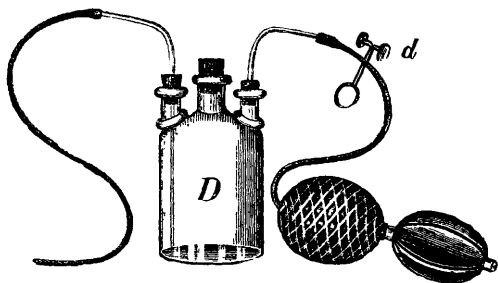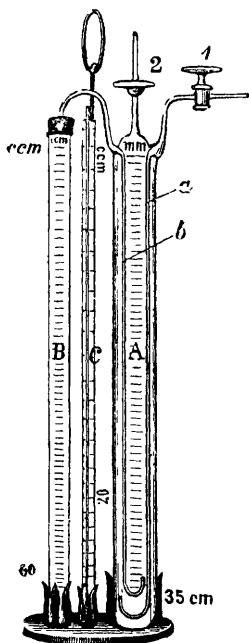
The apparatus is intended for collecting any gas in the cylinder A. The tube a must be first emptied by rapidly passing through it a current of a gas soluble in the liquid. The gas to be measured is then introduced and removed from the generating flask by a further current of the soluble gas. If, for instance, hydrogen is to be estimated in presence of carbonic anhydride, the cylinder A is filled with aqueous potash, which absorbs the carbonic anhydride whilst the hydrogen is collecting on the top, displacing an equal volume of liquid which, after

being expelled through the tube *b*, is measured in B. When great accuracy is wanted, the tube C is used; as soon as the gas has been collected in the cylinder A, the tube *b* is connected with the inner tube of C, which must be completely immersed in water or any other suitable liquid. If now from any cause a contraction of the gas in A should take place, a corresponding diminution of volume of liquid in C is noticed, which must then be deducted from the measured quantity of liquid in the tube B.

By means of the centimeter scale on A, the extra pressure inside can be ascertained. The volume of gas is read off in millimeters, and this corresponds with double the height of the column of liquid, the difference being regarded as extra water pressure, which may be reduced to mercury pressure by dividing by 13·6, and must then be added to the observed barometric pressure. The volume of gas ascertained by measuring the liquid in B is then, as usual, corrected for temperature and vapour tension as well as for pressure.

L. DE K.

Apparatus for Volumetric Analysis. By D. SIDERSKY (*Zeit. anal. Chem.*, **35**, 438—440).—The author has devised a stand, which carries two burettes and two bottles of standard solutions. The latter are Woulff's bottles with two necks, one neck carrying a tube which enters the top of the burette and terminates at the zero, the other is fitted with an elastic ball. On squeezing the ball, the pressure of the air drives the solution over into the burette, and on releasing the pressure, the excess of liquid above the zero is returned to the bottle, followed by air until the pressure is equalised. M. J. S.

Methods for the Estimation of Water. By S. L. PENFIELD (*Zeit. anorg. Chem.*, **7**, 22—32).—The author recommends for the estimation of water in minerals a modification of the plan employed by Brush in the analysis of sussexite (*Amer. J. Sci.*, **46**, 240). An ordinary hard glass tube, of about 6 mm. internal diameter, and 20—25 cm. long, is closed at one end. The substance to be examined is introduced into the bottom of this, and, the tube being held horizontally, the closed end is gradually and strongly heated. The water driven off condenses in the cool part of the tube, and as the residue is often hygroscopic, the tube is best sealed just above the substance, and drawn off. The remainder is allowed to cool, cleaned outside, weighed, the condensed moisture driven off by passing a current of air through the reheated tube, and the dry tube then again weighed. The difference of the two weighings gives the weight of the water lost by the substance under examination. The form of the tube may be altered, according to circumstances, by enlarging or contracting the closed end, or introducing bulbs for the more convenient retention of the condensed water. Whilst it is being heated, it is advisable to reduce all formation of currents in the tube to a minimum by attaching to the open end of the tube, by means of a short piece of rubber tubing, a small piece of glass tube drawn out to a capillary. If the temperature required to drive off the water is too high for a Bunsen burner or blowpipe, the closed end may be introduced into a blowpipe furnace, the projecting tube being protected

from radiant heat by screens. In this case, the portion of the tube in the furnace is protected by a roll of platinum foil, and by being surrounded with charcoal. By this method water may be correctly determined in substances where carbonic anhydride or other volatile substances are also driven off by heat. Where much carbonic anhydride is evolved, a correction at the rate of 0·0096 gram of water must be added for every gram of carbonic anhydride evolved, to compensate for the saturation moisture carried away by the gas. The method also gives very trustworthy results in cases where a substance has to be added to prevent the evolution of some volatile constituent, as, for instance, lime to prevent loss of sulphuric anhydride from ferrous sulphate.

The author also finds that moisture and carbonic anhydride may often be estimated together by heating the substance in a combustion tube in a current of dry air, and absorbing the moisture and carbonic anhydride evolved.   L. T. T.

Detection of Alkali Perchlorates in the Presence of Chlorides, Chlorates, and Nitrates. By F. A. GOOCH and D. A. KREIDER (*Zeit. anorg. Chem.*, **7**, 13—16).—If a mixture of an alkali perchlorate with zinc chloride is fused, chlorine is evolved; zinc chloride is preferable to manganous chloride, as it is not acted on by the air. The solution to be tested is evaporated to dryness in a test-tube, and then fused with anhydrous zinc chloride; if any perchlorate be present, chlorine will be evolved. Traces of chlorine are best detected by making a cap for the tube by cutting off the two bulbs of a straight drying tube, moistening the inside of the bulbs with potassium iodide solution, and resting these, the large opening downwards, on the top of the test-tube. In this way any evolved chlorine passes through the bulbs, and the least trace liberates iodine, which may be identified by means of starch solution. The author found that as little as a milligram of perchlorate could be readily detected in this way.

If chlorates or nitrates, or other substances likely to cause evolution of chlorine are present, they must, of course, be destroyed before making the test. The chlorates are easily destroyed by once evaporating with about 5 c.c. of concentrated hydrochloric acid. Nitrates are best destroyed by evaporation with 2 c.c. of a saturated solution of manganous chloride in concentrated hydrochloric acid, and subsequent re-evaporation with 1 to 2 c.c. of concentrated hydrochloric acid. The manganese must then be removed by sodium carbonate.
                                     L. T. T.

Volumetric Estimation of Iodine, Iodic acid, and Iodates. By D. VITALI (*Chem. Centr.*, 1894, i, 696; from *Boll. chim. farm.*, 1894, No. 4, *Apoth. Zeit.*, **9**, 164).—From the equation $SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4$, it will be seen that, when sulphurous anhydride is added to a solution of free iodine, four equivalents of acid are formed for every two atoms of iodine; hence if the resulting mixture is titrated with normal soda, 1 c.c. of the latter will correspond with $\dfrac{2 \times 127}{1000 \times 4} = 0\cdot0635$ gram of iodine originally present. In the actual

process, sulphurous acid solution is added to the iodine solution, until the colour of the latter is nearly gone ; some starch solution is then added, and more sulphurous acid, until the blue colour is just discharged ; the acid liquid is then titrated with normal soda solution. The original iodine solution must be neutral, and the sulphurous acid solution must contain no sulphuric acid. Free bromine and chlorine can also be estimated in this way, the sulphurous acid being added until a drop of the solution gives no colour with a solution containing starch and potassium iodide.

Iodic acid and iodates can be estimated in the same way; each molecule gives rise to the formation respectively of 7 and of 6 equivalents of acid, as is evident from the equations $3SO_2 + HIO_3 + 3H_2O = HI + 3H_2SO_4$; $3SO_2 + KIO_3 + 3H_2O = KI + 3H_2SO_4$.

C. F. B.

Iodometric Studies and the Constitution of Iodide of Starch. By C. LONNES (*Zeit. anal. Chem.*, **35**, 409—436).—In the presence of a metallic iodide, starch is coloured blue by a much smaller quantity of iodine than when iodides are absent. This is especially noticeable when there are alkali carbonates in the solution, and accounts for the fact that the use of normal sodium carbonate for neutralising an arsenious acid solution does not interfere with the accurate titration of the arsenic by iodine dissolved in potassium iodide. The explanation put forward by Fresenius, that the partial conversion of the normal into the hydrogen carbonate renders it incapable of hindering the formation of the blue compound, is shown to be devoid of foundation. Extreme accuracy in the titration of arsenious acid can be attained by using normal ammonium carbonate for making the solution alkaline, and adding potassium iodide with the starch paste. Using a N/1000 iodine solution a satisfactory estimation can be made with half a milligram of arsenious acid.

When iodine is added to an alkali (whether hydroxide or carbonate), its conversion into iodate and iodide is not immediately complete. A portion remains uncombined, as is evidenced by the yellow colour of the solution, and another part produces hypoiodite. The amount remaining free varies with the kind and proportion of alkali, and decreases with lapse of time. It is greatest with the hydrogen carbonates, and smallest with the hydroxides. It is much augmented by the addition of potassium iodide. The hypoiodite exhibits greater stability in presence of alkali hydroxides (potash or ammonia) than in solutions of carbonates. It is this formation of hypoiodite which falsifies titrations of iodine by thiosulphate solutions containing alkali, since hypoiodite oxidises thiosulphate to sulphate (see also Topf, Abstr., 1887, 688). The addition of potassium iodide does not hinder this action. The addition of ammonium carbonate or other alkali to thiosulphate as a preservative is therefore undesirable, and all titrations of iodine by thiosulphate should take place in acid solutions.

As regards the constitution of the blue compound, it is shown that whereas the addition of mercuric chloride prevents the production of the blue colour, this is at once restored by the addition of potassium or hydrogen iodide, in quantity a little larger than suffices for

the conversion of the mercury into iodide. This indicates that the presence of a soluble iodide is necessary to the formation of the blue compound. Although the blue compound is obtained when iodine free from hydriodic acid is added to starch, its formation is not instantaneous, and part of the iodine is combined in a form in which it is not capable of oxidising thiosulphate. When the blue compound is formed in a solution containing both hydriodic acid and free iodine, 1 equivalent of the former is removed from solution with 4 equivalents of the latter. Finally, estimations of the iodine in washed blue compounds showed that one-fourth of it was present in a condition in which it was incapable of oxidising arsenious acid. Although these results are not absolutely concordant, they confirm the view of Mylius, that hydriodic acid is an essential constituent of the blue compound.   M. J. S.

Estimation of the Sulphur in Earth-Nut Oil. By H. KAST and F. LAGAI (*Zeit. anal. Chem.*, **35**, 470 ; from *Dingl. polyt. J.*, **284**, 71).—0·5 to 1 gram of substance is mixed with 100 c.c. of fuming nitric acid, and 10 grams of potassium chlorate is gradually added. After 1—2 hours at the ordinary temperature, the mixture is heated carefully on the sandbath for 12—15 hours, until oily drops are no longer visible. It is then repeatedly evaporated to dryness with strong hydrochloric acid, filtered from resin, and the sulphuric acid in the filtrate estimated as usual. Carius' method gives low results.
                                                                        M. J. S.

Estimation of Total Sulphur in Urine. By H. SCHULZ (*Pfluger's Archiv*, **57**, 57—61).—The usual manner of estimating the total sulphur in urine is to evaporate to dryness, and fuse the residue with sodium carbonate and nitre. There is probably loss in this way from the passing off of sulphurous anhydride. The method here described obviates this difficulty by collecting in water all fumes during evaporation and fusing. The apparatus devised for this purpose is figured.   W. D. H.

Estimation of Total Nitrogen in Urine by the Schneider-Seegen Method. By F. VOIT (*Zeit. Biol.*, **31**, 168—180).—The Kjeldahl method of estimating nitrogen has the disadvantage of taking a long time to perform; this is not the case with the older method of Schneider-Seegen. The latter, however, has lately fallen into discredit, and the object of the present paper is to show that it is quite as accurate as Kjeldahl's process. The method is a modification of that of Will and Varrentrapp, adapted for the examination of urine, and briefly consists in heating the urine with soda-lime, and thus obtaining all the nitrogen in the form of ammonia.
                                                                        W. D. H.

Analysis of Commercial Sodium Nitrite. By MASSON (*J. Pharm.*, [5], **30**, 41—42) —Five grams of the nitrite are dissolved in 500 c.c. of water; 50 c.c. of this solution is transferred to a flask (1½ litres capacity), diluted to 1 litre, and then titrated with a standard solution of potassium permanganate (10 grams per litre) in the following manner. A few drops of a 10 per cent.

sulphuric acid is dropped into the solution, the flask is shaken, and some potassium permanganate is immediately added; this alternate addition of acid and permanganate is continued until the pink colour becomes permanent, when the flask is at once heated over a gas flame until the colour fades; potassium permanganate and acid are then immediately added, and the flask heated anew. This cycle of operations is continued as long as the permanganate is decolorised by the solution, the final temperature of which will approximate to the boiling point. A. G. B.

Reduction of Arsenic acid by the Action of Hydrochloric acid and Potassium Bromide. By F. A. GOOCH and I. K. PHELPS *(Amer. J. Sci.,* [3], **48**, 216—218).—It has been shown in a former paper (this vol., ii, 331) that arsenic acid may be readily reduced and volatilised as chloride by distilling with hydrochloric acid and potassium iodide. The authors now propose to use potassium bromide instead. The apparatus used is essentially the same as before, but when the distillate is condensed, the liberated bromine will reoxidise the arsenic. This, however, may be prevented by adding some stannous chloride, and the arsenic may then be at once precipitated with hydrogen sulphide. The large amount of free acid prevents precipitation of the tin, and also of any trace of antimony which may be present. L. DE K.

Decomposition of Silicates by Ferrous and Manganese Oxides. By R. SACHSSE and A. BECKER *(Landw. Versuchs-Stat.,* **45**, 147—151).—It was previously shown (Abstr., 1893, ii, 243) that when silicates are ignited with ferrous oxide, a portion of the oxide acts on the silicate, and can no longer be reduced by hydrogen to metallic iron. More exact experiments were made with ferrous oxide and with manganese oxide, as it was hoped that it might be possible, owing to the different behaviour of the various silicates, to effect a separation of single soil constituents, but inasmuch as all silicates, and even quartz, are more or less attacked, no separation could be made in this manner.

The results of comparative experiments, in which kaolin, orthoclase, and quartz were ignited with ferrous and manganese oxides respectively, show that manganous oxide is a stronger reagent than ferrous oxide. This does not, however, prevent the partial reduction of ferrous oxide in presence of an excess of manganous oxide.

When iron-kaolin (prepared by precipitating ferric chloride solution with water glass) was mixed with manganese dioxide and ignited in a current of hydrogen, only a small amount of metallic iron was formed. N. H. M.

Volumetric Separation of Hydroxides, Carbonates, and Bicarbonates. By C. KIPPENBERGER (*Zeit. angw. Chem.*, 1894, 495—501).—The author recommends using some new indicators, the advantage of which will be perceived by perusing the table below :—

By	Hæmatoxylin.	Galleïn.	Alkannin.	Gentiana blue.	Lyons blue.	Poirrier blue.
Hydroxide	Blue	Blue	Blue	Dark blue	Red	Red.
Alkali { carbonate	Red	Blue changing to red	Blue	Red	Red	Red in strong solution; blue in dilute.
{ bicarbonate	Red	Red	Red	Blue	Blue	Blue.
Barium, Strontium, or { carbonate	Red	Red	Red	Blue	Blue	Blue.
Calcium { bicarbonate	Red	Red	Red	Blue	Blue	Blue.
Magnesium { carbonate	Blue	Blue	Blue	Blue	Red }	Blue.
{ bicarbonate	Red	Red	Red	Blue	Blue }	Blue.

In titrating carbonates, it must be borne in mind that during the first stage half the alkali passes into bicarbonate. This, of course, is only true when the standard acid is very dilute and is added in very small portions at a time. To better prevent loss of carbonic acid, the titration is performed in a narrow cylinder provided with a glass stopper. The reagents are generally used in alcoholic solutions.

L. DE K.

Estimation of Sodium Hyposulphite. By E. H. EKKER (*Rec. Trav. Chim.*, **13**, 37—45).—The methods at present in use for the estimation of the amount of sodium hyposulphite in its solutions do not give very satisfactory results, and the author has therefore reinvestigated the subject. He finds that potassium ferricyanide is a very suitable reagent for the purpose, as it is not affected by sodium hydrogen sulphite, but is at once converted by the hyposulphite into a ferrocyanide. The liquid to be tested is placed in a flask from which all air is driven out by hydrogen, nitrogen, or carbonic anhydride, any free acid neutralised with soda, and a small quantity of ferrous ammonium sulphate added as indicator; the standard solution of potassium ferricyanide is then added until the solution assumes a blue colour.

In order to determine the nature of the action which takes place, the author dissolved varying quantities of pure zinc in solutions of sodium hydrogen sulphite; on estimating the quantity of potassium ferricyanide required to oxidise the hyposulphite formed, he found that 1 mol. of ferricyanide was equivalent to 1 atom of zinc. According to Schützenberger, sodium hyposulphite has the formula $NaHSO_2$, and its formation is represented by the equation

$$3NaHSO_3 + Zn = NaHSO_2 + ZnNa_2(SO_3)_2 + H_2O,$$

whilst, according to Bernthsen, it has the composition $Na_2S_2O_4$, and is formed as follows.

$$4NaHSO_3 + Zn = Na_2S_2O_4 + ZnNa_2(SO_3)_2 + 2H_2O.$$
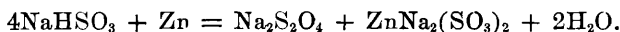
In order to obtain evidence as to which of these views is correct, known quantities of sodium hydrogen sulphite solution were well shaken with zinc, in the cold, until no further action took place, and the quantity of dissolved zinc was then estimated. It was found that 1 gram of sodium hydrogen sulphite is equivalent to 0·154 gram of zinc, which agrees with the requirements of the second of the above equations, thus affording renewed confirmation of Bernthsen's formula for hyposulphurous acid. H. G. C.

Assay of Zinc Dust. By F. MEYER (*Zeit. angw. Chem.*, 1894, 435).—The author believes that his apparatus is preferable to the one proposed by Bach (this vol., ii, 332—400), and that it may also be used for other purposes, such as the estimation of carbonic anhydride in carbonates. In this case, the dilute sulphuric or hydrochloric acid should be first saturated with carbonic anhydride, best by introducing a small quantity of sodium hydrogen carbonate. The apparatus without the generating flask may also be used for collecting and measuring any gas under atmospheric pressure, provided its volume is between 260 and 400 c.c. L. DE K.

Employment of Mercuric Oxide in Analysis. By E. F. SMITH and P. HEYL (*Zeit. anorg. Chem.*, **7**, 82—90).—The use of mercuric oxide has been recommended by Berzelius and by Volhard (*a*) for precipitating some of the metals from their solutions, and (*b*) for converting chlorides, sulphides, &c., into oxides for weighing. The

authors have investigated this subject, to determine in which cases this reagent can be advantageously used.

For preparing oxides for weighing, the precipitate (sulphide, &c.) is dissolved in a little hydrochloric acid, evaporated to a small bulk, and introduced into a crucible; excess of mercuric oxide is then added, and some strewn over the moist inner sides of the crucible, the whole is slowly dried on a hot plate, and finally heated strongly, to drive off all mercuric chloride and oxide. In this way, zinc sulphide may be readily and quickly converted into oxide for weighing. Cadmium gives good results if care is taken to well powder the sides of the crucible, and not to allow the crucible to become red-hot until the fumes of mercuric oxide have entirely disappeared; otherwise, some of the cadmium chloride may be volatilised before its conversion into oxide. Manganese and nickel sulphides, and bismuth oxychloride give good results. Cobalt does not give a sufficiently definite oxide to be satisfactory, the final product varying in composition between C_3O_4 and Co_2O_3, according to the temperature, &c.

For separating metals by precipitation, mercuric oxide may safely be used to separate iron from manganese in cold solutions, although the first precipitate should be redissolved and reprecipitated to ensure freedom from traces of manganese. It may be used as a quick, approximate method of separating iron from nickel or cobalt, if absolute accuracy is not required. Chromium is also precipitated from its cold solutions. Zinc, nickel, cobalt, uranium, berylium, cerium, and lanthanum are only partially precipitated in the cold.

<div align="right">L. T. T.</div>

Reaction of Copper Salts. By H. Thoms (*Zeit. anal. Chem.*, **35**, 464; from *Pharm. Centr.*, **31**, 31).—If to a solution of cupric sulphate in 200,000 parts of water, which is too dilute to give a visible coloration with potassium ferrocyanide, potassium iodide is added, a yellow coloration is produced, becoming violet with starch paste. The latter coloration is visible even with 500,000 parts of water.   M. J. S.

Quantitative Analysis by Electrolysis. By A. Classen (*Ber.*, **27**, 2060—2081).—A description is given, accompanied by plans and a sketch, of the manner in which the private laboratory, and a bench in the inorganic laboratory, are fitted up for electrolysis at Aix-la-Chapelle. At the bench, 24 electrolyses can be simultaneously carried out, and the current in each electrolytic cell can be measured by means of an ampère-meter common to the set. The usual method of measuring the current with a gas voltameter before the electrolysis is commenced is very faulty. The author uses an ampère-meter, which can be thrown into circuit during electrolysis by adjusting a copper bridging-wire between two mercury cups. When the measurement is made, the bridge is removed and connection made, so as to cut off the ampère-meter, but this time by means of a bridge having a resistance just equal to that of the meter; the current in the circuit thus remains equal to that at the time of measurement. The current is not quoted, but the "current-density," or the number of ampères per 100 sq. cm. of surface of the electrode. The solutions used were commonly made by adding ammonium, or occasionally potassium

oxalate to a solution of the salt of the metal, some free oxalic acid being also usually added. In the case of antimony, however, sodium sulphide was added, and, in the case of silver, potassium cyanide. The deposits were dense and metallic. With lead, the electrolysis was carried out in the presence of nitric acid only, and the deposit of peroxide weighed as such. With manganese, it was done in the presence of acetic acid only, and the precipitate of peroxide was ignited and weighed as Mn_3O_4. In the case of mercury, tin, antimony, lead, and manganese, it was found expedient to use, not a polished platinum dish, but one the surface of which had been made matt by means of a sand blast; the deposit often adhered to this, when it would not adhere to a smooth surface. Below are given details of current-density in ampères, difference of potential of the electrodes in volts, temperature, and duration of the electrolysis as employed in depositing various metals.

	Current-density, ampères.	Diff of potential, volts.	Temp.	Time, hours.
Copper	1·0—0·35	3·2—2·5	58—60°	2—2½
Cadmium	1 0—0·5	3·4—2·75	68—76	3—3½
Zinc...........	1·0—0·5	4·8—3·5	55—60	2
Iron...........	1·5	3—4	20—15	½—¾
Nickel........ ⎱ Cobalt........ ⎰	1·0	3·0—3·5	60—70	2¼—2¾
Mercury........	1·0—0·2	4·7—2·6	23—37	1½—5¼
Silver	0·5—0·2	4·8—3·3	20—30	1¾—5
Tin	0·3—1·0	3·2—4·2	25—30	5¾—6¼
Antimony	1·5—0·3	1·85—0·85	25—60	2—17½
Lead	1·65—1·45	2·5—2 4	60—65	1—1¼
Manganese	0·3	4·9—4·3	50—68	3

Similar details are also given for the separation of lead and copper, copper and iron, antimony from arsenic and from tin, copper from nickel and from cobalt, iron from aluminium and from chromium, and for the simultaneous deposition of iron and cobalt and of iron and nickel. The methods used are already well known.   C. F. B.

Colorimetric Estimation of Minute Quantities of Lead, Copper, Tin, and Iron. By E. R. Budden and H. Hardy (*Analyst*, **19**, 169—175).—The authors having tried the various processes in use for the colorimetric estimation of traces of these metals in m neral waters, lemonades, &c., came to the following conclusions.

That in determining traces of metals by the hydrogen sulphide process (compare Abstr., 1893, ii, 242, 599), it is, above all, necessary to follow strictly the same order in the addition of the reagents, and, as closely as possible, to use always the same quantity of the reagent, both in the actual experiment and in the preparation of the solution used for the comparative determination. That all the conditions of experiment should be similar; for instance, in testing a lemonade, the liquid for comparison should contain the same amount of sugar, acid,

&c. Even the amount of carbonic anhydride in effervescing beverages exercises a slight influence on the reaction. The authors promise further experiments and invite co-operation. L. DE K.

Estimation of Manganese, Magnesium, Zinc, Cobalt, and Nickel by Classen's Oxalate Process. By G. NASS (*Zeit. angw. Chem.*, 1894, 501—508).—Classen recommends adding a solution of potassium oxalate in excess and then precipitating the metallic oxalate by boiling with excess of acetic acid. The precipitate is then washed with a mixture of alcohol and acetic acid and at once ignited. The author, having tried the process with both potassium and ammonium oxalate, finds that it is perfectly useless for manganese, cobalt, and nickel, but that good results are obtained with magnesium and zinc.

L. DE K.

Estimation of Ferrous Iron in Silicates. By J. H. PRATT (*Amer. J. Sci.*, [3], **48**, 149—151).—The author dissolves the mineral in a boiling mixture of hydrofluoric and dilute sulphuric acids. To prevent oxidation, the solution is effected in a current of carbonic anhydride. The apparatus used consists of a Rose's ignition crucible, which must, however, be entirely made of platinum. After cooling, the liquid is transferred to a beaker or dish, and titrated with permanganate. The test analyses are very satisfactory. L. DE K.

Separation of Bismuth, Zinc, and Nickel by Hydrogen Peroxide. By P. JANNASCH and E. ROSE (*Ber.*, **27**, 2227—2231; compare Abstr., 1892, 537; 1893, ii, 492; this vol., ii, 32, 71).—Bismuth may be separated from zinc or nickel by pouring a solution of the nitrates of the metals in 5 c.c. of nitric acid and 50 c.c. of water into a mixture of 25 c.c. of 3—4 per cent. hydrogen peroxide and 15 c.c. of concentrated ammonia. Under these circumstances, the bismuth is completely precipitated as the hydrated peroxide, which is then collected and washed, first with dilute ammonia, finally with cold water. Only traces of zinc or nickel are precipitated along with the bismuth, so that, unless exceptional accuracy is required, it is not necessary to redissolve the precipitate and repeat the separation. The dried precipitate is removed from the filter paper, the latter carefully incinerated, and the ash treated with nitric acid; the precipitate is then added to the ash, and the whole carefully heated, a platinum crucible being used. The silica, which is usually present in hydrogen peroxide to the extent of about 0·006 gram per 50 c.c., is precipitated along with the bismuth, and must be allowed for.

The zinc or nickel is determined in the residue obtained by evaporating the filtrate after it has been carefully ignited to remove ammonium salts.

The authors have found that ammonium persulphate may often be employed as a reagent instead of hydrogen peroxide, but that it is not so convenient. A. H.

Rapid Detection of Tin. By G. DENIGÈS (*J. Pharm.*, [5], **30**, 207—212).—Various organic compounds are capable of immediately producing a blue coloration in a solution of sulphomolybdic acid

(ammonium molybdate, 10 grams; water, 100 c.c.; pure sulphuric acid, 100 c.c.). Among inorganic compounds, hypophosphites in hot solution, and hyposulphites, ferrous salts, cuprous salts, and stannous salts, at the ordinary temperature, produce the blue colour immediately.

Notwithstanding the presence of these other reducing agents in a solution, tin may be rapidly detected by the following method. Several drops of the suspected solution is placed on a piece of platinum with a drop of sulphuric acid, and a piece of zinc is brought in contact with the platinum underneath the surface of the liquid. After a minute or two, the platinum is washed with water, 4 or 5 drops of hydrochloric acid are dropped upon the spot, and the liquid evaporated to dryness at a gentle heat. 3 or 4 drops of water are then added to the residue, left there for some seconds, and 1 or 2 drops of the solution thus formed is poured into 2 or 3 drops of the sulphomolybdic acid; an instantaneous blue coloration indicates that tin must have been on the platinum, for, owing to the insolubility of cuprous chloride, this will not be dissolved by the water.

In alloys, tin may be rapidly detected as follows. Some particles of the alloy are placed in a capsule with a dozen drops of hydrochloric acid, which is then evaporated to dryness at a gentle heat. A few drops of water is now placed on the residue, and 1 c.c. of a nearly boiling solution of cacothéline is added. If tin be present, an amethyst colour is produced, which becomes blue with alkali in the absence of air, and green in the presence of air. The cacothéline solution is prepared by dissolving 0·5 gram of brucine in 5 c.c. of cold nitric acid in a flask, adding 250 c.c. of water, boiling for 10 to 15 minutes, and making up the volume of the cooled liquid to 250 c.c. If the tin is present in very small quantity, the amount of this reagent added should be limited to 4 or 5 drops; ferrous and cuprous salts do not yield the reaction. One-twentieth of a milligram of tin can be detected in a drop of liquid by this test.

Since metastannic acid is readily reduced to tin in the presence of zinc and hydrochloric acid, it can be readily identified by placing it on a sheet of zinc and moistening it with hydrochloric acid; the spot of zinc, on which the tin has been thus deposited, may be dissolved in acid and the tin detected by the tests described above.

A. G. B.

Separation of Tin from Antimony. By MENGIN (*Compt. rend.*, **119**, 224—226).—The alloy containing tin and antimony is treated with nitric acid, which dissolves the other metals and converts the tin and antimony into insoluble oxides, which are washed, heated, and weighed together. The oxides are then mixed with a plate or ball of tin and dilute hydrochloric acid, the liquid being gently heated for a few hours with occasional agitation. When all trace of the oxides has disappeared, the reduced antimony is collected on a weighed filter, washed with water and alcohol, dried, and weighed. The tin oxide has been converted into soluble chloride.

C. H. B.

Reduction of Vanadic acid by Tartaric acid and its Titration in Alkaline Solution with Iodine. By P. E. BROWNING (*Zeit.*

anorg. Chem., **7**, 158—160).—The solution of van idic acid is boiled with an excess of tartaric acid until it acquires a beautiful blue colour; it is then mixed with excess of potassium hydrogen carbonate, cooled, and treated with excess of standard iodine solution. When the blue coloration of vana lium tetroxide has disappeared, the excess of iodine is titrated with a solution of arsenious acid until the colour of the iodine is just discharged, finally the blue coloration should be obtained when a few drops of iodine solution and starch are added.

The results agree very well with those obtained by reduction with sulphurous acid and titration with permanganate.   E. C. R.

Analysis of Gold Ores. By S. Cotton (*J. Pharm.*, [5], **30**, 85—87).—1 kilo., or more, of the ore is finely powdered, roasted at a dull red heat to expel sulphur and arsenic, and made into a cream with water; 100 grams of mercury is added and the whole is shaken from time to time. After two days, 100 grams of potassium cyanide is added, and the intermittent shaking is continued for another two days. The mixture is dried, and the mercury, which now contains all the gold, is separated, partly directly and partly by washing, and the greater portion of the metal dissolved by nitric acid; the remainder is expelled by heat in an open crucible. The gold is thus left ready to be weighed. The process is capable of estimating quantities of gold, which cannot be determined by the usual lead assay.
          A. G. B.

Modifications of Romijn's Apparatus for the Estimation of Dissolved Oxygen in Water. By J. C. Boot (*Rec. Trav. Chim.*, **13**, 88—92; compare Romijn, this vol., ii, 28).—The apparatus is shown in Fig. 1. The flask A has a capacity of about 4 litres, and is fastened by bands of copper (C) to the leaden sinker B, which is mounted on a wooden plate V. The pipette H is attached to A by the copper frame KL, has a three-way cock at F, and is connected by rubber tubing to D, which is closed with a stopper attached to a string. The apparatus is lowered to the required depth, and the stopper removed from D, the flask and pipette quickly fill with water, the air escaping by the tube T. The water in the pipette is used to estimate the oxygen, that in the flask for the determination of the ammonia, &c. Fig. 2 represents an improved form of pipette (H in Fig. 1). A and B are two three-way taps, the bulb C contains about 10 c.c., its capacity between the fiducial marks M and N being accurately determined, the tube R communicates at S with the sodium hyposulphite solution, the other tube is connected with a supply of hydrogen. The sodium hyposulphite solution is introduced by turning the taps into the position shown in the figure. When the solution reaches the mark M, B is closed, and A is turned so that the bulb communicates with the source of hydrogen, the pipette is then attached to R and the solution allowed to flow through P, the liquid being afterwards drawn back to the mark N. The iodine solution is introduced in a similar manner.

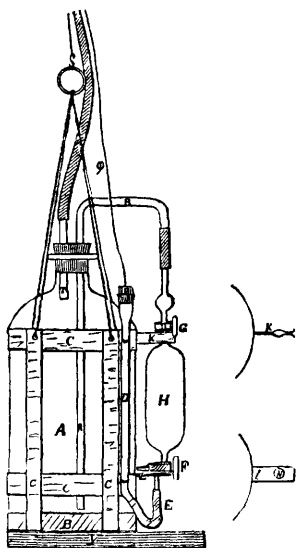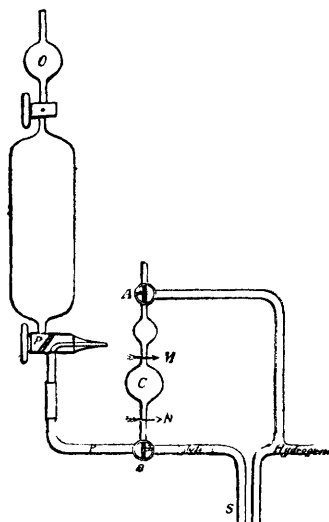This apparatus allows water to be obtained from any depth, in

FIG. 1.

FIG. 2.

quantity sufficient to admit of the estimation of all the constituents; it is much easier to manipulate than Romijn's, and the pipette, being free from adhering water and dirt, ensures greater accuracy.
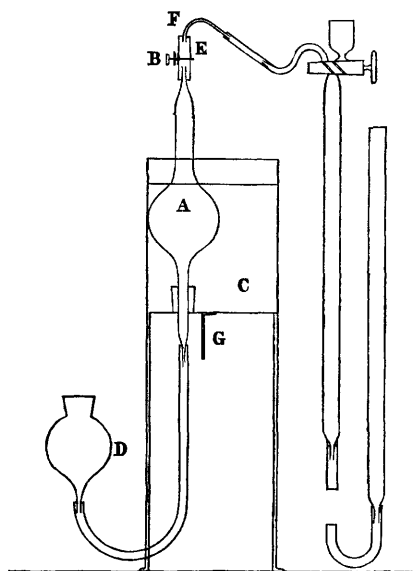
J. B. T.

Apparatus for Collecting Samples of Water some Distance beneath the Surface. By W. T. BURGESS (*Chem. News*, **70**, 54) — This apparatus is for obtaining samples for bacteriological examinations. A partially exhausted glass tube, of 6 c.c. capacity, drawn out at the top to a narrow tube and at one point to a very fine capillary, is supported in a weighted wire holder and lowered into the water; at any desired depth, a jerk of the wire by which the tube is lowered releases a spring attached to the holder, which, flying round, breaks off the tube at the capillary. The tube fills in a few seconds, and is then drawn up and sealed. D. A. L.

Apparatus for the Extraction of Gases Dissolved in Water. By S. HARVEY (*Analyst*, **19**, 121—123).—The apparatus consists of a globular, spindle-shaped glass vessel A. having two opposite tapering necks, 13—14 in. long between the two extremities, the globular part being $3\frac{1}{4}$ or $3\frac{1}{2}$ in. in diameter. The upper neck is somewhat enlarged, tapering gradually, the lower is narrow and cylindrical; both end in a capillary bore bulbous at the end, to enable the rubber tubing to be securely affixed. The upper one has a short length of small-bore pressure tubing, securely tied and furnished with a screw clamp B. The apparatus is used as follows:—In the first place, the exact

37—2

capacity from end to end is ascertained. It is then filled with the sample of water, the clamp B is closed, and the vessel carefully fixed upright in a tin water-bath C, 6 in. in diameter and 7 in. high, standing on legs 12 in. high, and having an opening in the bottom closed by a perforated cork; the latter is so arranged that whilst the lower stem of the spindle projects 2 in. below the bottom, the globular part is immersed in the bath. The clamp is now opened, and about one-third of the water allowed to run into a measured vessel. This amount deducted from the total gives the amount experimented on. The lower end of the spindle has now one end of a 2 ft. piece of small-bore pressure tubing slipped over it and secured. This tubing has a mercury reservoir D at the other end, and the latter is suitably supported.

Mercury is now poured into the reservoir, the clamp B is again opened, and the air, together with any bubbles, driven out, the water being allowed to follow to the upper end of the rubber tube E. After closing the clamp, a nitrometer having a bent capillary tube, F, affixed to the beak, is filled with mercury, and this is forced to the end of the capillary tube, which is now thrust into the top of the rubber tubing and secured. The reservoir is lowered and the clamp cautiously opened in order to run a little mercury over sufficiently far to reach the lower end of the capillary tube. The clamp is now closed, the bath filled with cold water, and heat applied. To prevent the latter injuring the lower end of the spindle, a metal screen G is riveted on to the bottom of the bath so as to screen the glass from the flame, and for the same reason the hole in the bath is at one side to allow sufficient space for heating.

Under the diminished pressure, the water in the globe soon boils vigorously and without bumping, and the expelled gases collect in the upper stem. After two hours, the reservoir may be raised, the clamp B opened, and the gases passed into the nitrometer, taking care not to admit any water. The clamp is again closed, the reservoir lowered, and the operation continued to collect any further traces of gas. By raising the reservoir, any residual gas may be driven completely into the nitrometer, where it is subjected to measurement and absorption.

L. DE K.

The Relation of Saccharimeter Degrees to Angular Degrees. By E. RIMBACH (*Ber.*, **27**, 2282—2285).—One scale division on the

Ventzke quartz wedge saccharimeter is usually taken as equal to 0·3455° or 0·3465° of rotation for sodium light. The author has redetermined this ratio, and finds that it increases slightly as the concentration of the sugar solution increases; he uses, as the source of light, either an ordinary gaslight or an Auer lamp with a dichromate screen. For cane sugar and glucose the mean value of the ratio is 0·344; the ratio is practically the same for solutions of santonin in chloroform and of camphor in alcohol. W. J. P.

Gravimetric Estimation of Sugar by Fehling's Solution. By C. KILLING (*Zeit. angw. Chem.*, 1894, 431—433).—The author states that in the otherwise excellent process of Märcker and Allihn, everything depends on the quality of the asbestos used. As the peculiar kind recommended bids fair to become very scarce, or perhaps to altogether disappear from the market, the author has again taken to the old plan of collecting the cuprous oxide on a filter. The *modus operandi* is as follows.

The filter containing the cuprous oxide is dried at 100°, the contents then transferred to a weighed dish, cooled in a desiccator, and weighed. The filter is now burned in a weighed porcelain crucible, ignited over the blow-pipe, and the cupric oxide finally weighed. The result will be, however, somewhat too high, as the filter paper always absorbs some copper from the Fehling's solution which washing fails to remove. This quantity is, however, fairly constant, and may be once for all determined by a blank experiment.

L. DE K.

Estimation of Sugar by Fehling's Solution. By A. PRAGER (*Zeit. angw. Chem.*, 1894, 520—521).—The author (see preceding abstract) prefers to operate as follows :—The cuprous oxide is collected on a double filter, washed and dried. The precipitate is now as much as possible detached from the filter, and transferred to a piece of glazed paper. The filter is incinerated in a platinum crucible, and the ash well pressed with a platinum wire. The cuprous oxide is transferred to the crucible and the ignition continued over a small flame at first, actively stirring all the while. After heating the covered crucible with the full flame for a few minutes, it is cooled and weighed. The outer filter is ignited so as to estimate the amount of copper absorbed by the paper. L. DE K.

Estimation of Sugars by Fermentation. By LASCHÉ (*Bied. Centr.*, **23**, 551—552; from *D. Bierbrauer*, **21**, 1210—1213).—In the estimation of sugar with Fehling's solution, high results may be obtained, owing to the action of the Fehling's solution on substances which are not sugars. It is, moreover, sometimes desirable to estimate single sugars. It is therefore proposed to employ certain forms of yeast which ferment one or more sugars. By fermenting, for instance, wort (500 c.c.) with Saaz yeast (2 5 grams), the amount of maltose, dextrose, and saccharose can be determined, Saaz yeast being unable to ferment the substances known as maltodextrin, or isomaltose. If instead of Saaz yeast, *Saccharomyces apiculatus* is employed, the amount of dextrose alone is obtained.

In carrying out investigations of this kind, it is necessary to know the properties of the various yeasts : that *Saccharomyces apiculatus* will only ferment sugars like dextrose; *Saccharomyces Joergensenii*, dextrose and saccharose; Saaz yeast, dextrose, saccharose, and maltose ; and that Frohnberg yeast decomposes all those sugars and isomaltose as well. *Saccharomyces Kephir* may be employed for the estimation of lactose.   N. H. M.

Examination of Urine for Small Quantities of Sugar. By A. H. ALLEN (*Analyst*, **19**, 178—184).

—To detect small quantities of sugar in urine, the author operates as follows :—7 to 8 c.c. of the sample is heated to boiling in a test-tube, and 5 c.c. of solution of copper sulphate—as used to make Fehling's solution—is added. This precipitates nearly all the uric acid, xanthine, hypoxanthine, phosphates, &c. When nearly cold, 1 to 2 c.c. of a saturated solution of sodium acetate is added, which will render the precipitation complete. After filtering, 5 c.c. of the usual alkaline tartrate mixture is next added, and the mixture boiled for 15 to 20 secs. In the presence of more than 0·25 per cent. of sugar, separation of cuprous oxide occurs before the boiling point is reached, but with smaller proportions precipitation takes place during the cooling of the solution, which becomes greenish, opaque, and suddenly deposits cuprous oxide as a fine orange-yellow precipitate. The best qualitative test for traces of sugar is, however, the well-known reaction with phenylhydrazine.   L. DE K.

Reactions of Normal and Basic Lead Acetates with Sodium Carbonate, Sulphate, and Phosphate. By A. BORNTRAEGER (*Zeit. angw. Chem.*, 1894, 454—460).

—If normal lead acetate is cautiously precipitated with sodium carbonate, the filtrate is distinctly acid to delicate litmus paper ; but the author finds this to be due to carbonic and not to acetic acid. The filtrate also contains a little lead, which will, however, not be the case if the acetate has been precipitated with an excess of sodium carbonate.

If normal lead acetate, which always has a slightly acid reaction, is mixed with sodium sulphate, a neutral filtrate is obtained. The end of the reaction is not so marked as with sodium carbonate, and it is therefore difficult to avoid excess of the reagent. A large excess of the latter seems necessary for the complete precipitation of the lead.

Although lead acetate has but a feebly acid reaction, and sodium dihydrogen phosphate a decidedly alkaline one, the two salts when mixed in equivalent proportions give a strongly acid filtrate which contains only traces of lead and phosphoric acid. If a slight excess of sodium phosphate is used, a filtrate free from lead is obtained.

When basic lead acetate and sodium carbonate are mixed, a neutral filtrate is obtained which contains traces of lead if no excess of the reagent has been added ; traces of lead will, however, reappear on adding a large excess of the same.

From basic lead acetate and sodium sulphate, a neutral filtrate is obtained containing a small quantity of lead ; this may, however,

be reduced to a mere trace by using a fairly large excess of the reagent, and allowing this to act for 24 hours.

From basic lead acetate and disodium hydrogen phosphate, an acid filtrate is obtained, which will be free from lead if the phosphate be added in large excess and allowed to act for some 24 hours.

L. DE K.

Reactions of Normal and Basic Lead Acetates with Sodium Carbonate, Sulphate, or Phosphate in the presence of Invert Sugar. By A. BORNTRAEGER (*Zeit. angw. Chem.*, 1894, 521—528).— The author (see preceding abstract) has tried the reaction of normal and basic lead acetates with sodium carbonate, sulphate, and phosphate in the presence of invert sugar.

Sodium carbonate added in equivalent proportion does not completely precipitate the lead acetate. On adding an excess, part of the precipitate redissolves, but it gradually reprecipitates to a certain extent. The solubility is, however, not due to the invert sugar as such, but only to the levulose it contains, as dextrose has no solvent action.

Sodium sulphate, added in moderate excess only, leaves a trace of lead in solution, but a larger quantity precipitates the lead as completely as in the absence of invert sugar.

Disodium hydrogen phosphate also precipitates the lead completely.

Sodium carbonate added to a solution of basic lead acetate does not completely precipitate the lead, whilst an excess actually redissolves some of the precipitate; this, however, is reprecipitated to a certain extent after some time.

Sodium sulphate when added either in great or small excess does not completely precipitate the lead even on long standing.

Disodium hydrogen phosphate completely removes the lead from the sugar solution. L. DE K.

Reaction for Aldehydes : Differentiation of Aldoses and Ketoses. By A. VILLIERS and M. FAYOLLE (*Compt. rend.*, 119, 75— 77).—Carefully purified acetone has no action on a solution of magenta decolorised by sulphurous acid, but the removal of the last traces of aldehyde is extremely difficult. It follows that this reagent can be used for the detection of aldehydes in acetone ; it should be prepared without excess of sulphurous acid, and the experiments should be made in closed tubes. Methyl ethyl ketone gives no coloration with the reagent, but it is desirable that a large number of other carefully purified ketones should be examined.

The reagent can also be employed to distinguish between aldoses and ketoses. Glucose, invert sugar, and galactose produce a coloration as intense as with ordinary aldehyde, but levulose and sorbitol give no reaction. About 1 gram of sugar should be added to 10 or 12 c.c. of the reagent, which should be free from acid, since the latter interferes with the reaction.

Saccharose, maltose, and lactose give no coloration, but after several days, a coloration appears, probably in consequence of a

d·composition in presence of water with formation of aldehydic glucoses.   C. H. B.

Valenta's Acetic acid Test. By W. CHATTAWAY, T. H. PEAR-MAIN, and C. G. MOOR (*Analyst*, **19**, 147—150).—The authors have adopted the following method :—A short and somewhat thick test tube of about 4 in. × $\frac{1}{2}$ in., into which a well-fitting stopper has been ground, is chosen ; 2·75 grams of the fat is then weighed into the tube, and 3 c.c. of acetic acid of exactly 99·5 per cent. strength is measured from a burette, and added to the fat. The tube is then stoppered and placed in a beaker of warm water, increasing the heat until, after shaking. the contents become quite clear. The source of heat is then removed, and the tube is so placed that it is in the centre of the beaker ; the whole is then allowed to rest until the change from transparency to turbidity occurs, when the temperature is observed by means of a thermometer which has been previously attached to the test tube by a rubber band. The change is very well marked. It is of the utmost importance that the fat or oil—olive oil, for instance—should be entirely free from water. The fat should also not have been subjected to any over-heating.

The authors have tabulated the results of their experiments with a large number of oils and fats. As regards butter, figures varying from 39—29° were obtained, whilst " margarine " gave 97—94°. The test seems most useful when applied to butters, margarines, or mix-tures of the two.   L. DE K.

Turbidity Temperature of Oils and Fats with Glacial Acetic acid. By E. W. T. JONES (*Analyst*, **19**, 151—155).—The author (see preceding abstract) having noticed that even the presence of 0·2 per cent. of water in the acetic acid makes a serious difference in the turbidity temperature, proposes to check the acid with normal butter fat. To the best glacial acetic acid, water is carefully added until the turbidity temperature with the normal butter fat comes exactly at 60° ; the acid is then reserved for the testing.

It is also most important that the relative proportions of acid and fat should be strictly adhered to. The author uses special pipettes, a narrow one holding 3 grams of water at 15·5° for the acid, and wider ones, with wider orifices, delivering 3 grams of water for the fat. All oils or fats are measured at 50°.   L. DE K.

Stable Form of Hübl's Iodine Solution. By P. WELMANS (*Zeit. anal. Chem.*, **35**, 457 ; from *Pharm. Zeit.*, **38**, 220).—For pre-paring the solution of iodine with mercuric chloride, a mixture of acetic acid with an equal volume of ethylic ether or ethylic acetate is used. The solution is fit for use immediately, and retains its strength for a long time.   M. J. S.

Analytical Constants of Seal Oil. By A. C. CHAPMAN and J. F. ROLFE (*Chem. News*, **70**, 1—2).—The authors have tabulated some analytical *data* for seal oil. Six samples (also a sample of blown oil) which were undoubtedly genuine were tested for specific

gravity, insoluble fatty acids, melting points of the same, iodine and bromine absorptions, total acidity number, saponification equivalent, free (oleic) acid, and the " Reichert " figure. The processes are fully described, but present no novel features. The lighter coloured specimens were fairly constant as regards specific gravity (0·925—0·926) and the melting point (22—23°) of their insoluble acids. The other figures show great variation. L. DE K.

Microchemical Examination of Quinine. By H. BEHRENS (*Rec. Trav. Chim.*, **13**, 1—12).—In this paper, the author describes the microchemical reactions of the cinchona alkaloïds, quinine, cinchonine, quinidine, and cinchonidine, and describes a method by which small quantities of the last three may be readily detected in commercial samples of quinine. The paper does not admit of being shortly abstracted, and, for the details, reference must, therefore, be made to the original. H. G. C.

Estimation of the Alkaloïds in Strychnos Seeds. By C. C. KELLER (*Zeit. anal. Chem.*, **35**, 491—493; from *Apoth Zeit.*, **8**, 542). —Fifteen grams of the powdered substance is freed from fat by washing with ether in a tube plugged with cotton wool. The ethereal extract, amounting to 100 c.c., contains some alkaloïd, which must be recovered by shaking it with 15 c.c. of N/30 hydrochloric acid and washing out the acid with 10 c.c. of water. The exhausted residue is transferred to a vessel of 250 c.c. ; ether is added until the whole amount present is 100 grams, 50 grams of chloroform, and 10 grams of 10 per cent. ammonia solution are added, and the whole is shaken for half an hour. The acid solution is then added and again well shaken. When separation is complete, the ether chloroform solution is filtered, and 100 grams of it is evaporated in a tared conical flask. The residue is freed from chloroform, which it obstinately retains, by repeated evaporation with absolute alcohol, then dried at 95—100° and weighed. The purity of the alkaloïd may be verified by titration with iodoeosin as indicator. The proportion of chloroform to ether must be accurately observed. M. J. S.

Assay of "Cortex Granati." By W. STOEDER (*Chem. Centr.*, 1894, i, 606; from *Ned. Tydschr. Pharm.*, **6**, 39—44).—Gehe has stated that *cortex granati* only contains about 0·3 per cent. of alkaloïds. The author, however, has generally found 1 per cent., but in the root bark only, the other varieties yielding much less. Gehe's process of extracting the bark with a mixture of ether, chloroform, and ammonia, dissolving the crude alkaloïds in excess of standard sulphuric acid, and titrating back with an alkali is, however, quite trustworthy. L. DE K.

Analysis of Malt. By T. CROSSMAN (*J. Amer. Chem. Soc.*, **16**, [8], 559—565).—The author takes exception to some statements made by Miller on the analysis of malt (this vol., ii, 371). According to this chemist, the most important points from a brewer's view,

are : moisture, extract, diastatic power, and acidity.   The author
observes that these factors do not tell brewers of English beers
much, although they may be useful to those who brew German beer;
but when taken in conjunction with ready-formed sugars soluble in
water, the uncoagulable proteïds, free maltose, maltodextrin, or
dextrin and unmodified starch, the results give information of the
greatest possible value.   The moisture should be about 1 per cent.,
3 per cent. being regarded with suspicion.   The extract is usually
determined in England by Heron's method (*J. Soc. Chem. Ind.*, **7**,
259—276), and this has always given the author the greatest satis-
faction.   The diastatic capacity is best determined by Lintner's pro-
cess, but is not of much use unless the condition of the starch is
known.   The amount of ready-formed sugars should not exceed
17 per cent., calculated on the malt; it bears a relation to the pro-
portion of soluble uncoagulable proteïds, which, according to Moritz,
is represented by the factor 6·3.

After calling attention to the great importance of the estimation of
free maltose and maltodextrin, the author gives his own process for
the estimation of the unmodified starch (" steeliness ").   Fifty grams
of malt is mashed as usual, then boiled vigorously for one hour,
and then cooled to 150° F.; 50 c.c. of a cold-water extract (prepared
by soaking 50 grams of ground malt for four hours in 500 c.c. of water)
is now added, and the mash kept at 150° F. for one hour longer.   It is
then cooled down and made up to 515 c.c.   The gravity is taken,
allowance being made for the gravity caused by the cold-water extract.
The difference in solid matter between boiled mash and mash gives
the amount of unmodified starch, which should not exceed 7 per cent.

<div align="right">L. DE K.</div>

Estimation of Bilirubin in Bile.   By A. JOLLES (*Pflüger's
Archiv*, **57**, 1—57).—See this vol., ii, 466.

ERRATA.

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PART I.

Page | Line
411 | 2* *for* " G. MAZZARA " *read* " G. MAZZARON."
15 | 6 ,, " J. A. JESURIN " *read* " J. A. JESURUN."

PART II.

601 | 20* ,, " not fermented " *read* " fermented," and *for* " suffers'fermentation " *read* " not."

VOL. LXVI (ABSTR., 1894).

PART I.

73 | 14* }
234 | 23* } ,, " S. K. DZERZGOVSKY " *read* " S. K. DZIERZGOWSKY."

136 | 13* }
5* } ,, " nitrobenzal-β-dinaphtholmethane " *read* " nitrophenyl-β-di-
137 | 3 } naphtholmethane."

7 | ,, " metanitrobenzal-α-dinaphthylamine " *read* " metanitrophenyl α-dinaphthylamine."

184 | 1 }
7 } ,, " acetonecarboxylic acid " *read* " acetonedicarboxylic acid."

264 | 16* }
15* } ,, " ammonia " *read* " ammonium chloride."
14* }

411 | 13 ,, " NHPh·CS·NPh·N⦂CHMe₂ " *read* " NHPh·CS·NPh·N⦂CMe₂."
429 | 18 ,, " n-Phenylpyrazolene " ,, " n-Phenylpyrazolone."
451 | 26 ,, " C. ABERHART " *read* " C. EBERHARDT."

PART II.

6 | 10* In the original paper, sodium sulphate was erroneously stated to melt at 843°. The correct value is 899°.
123 | 6* *for* " C. PFLÜGER " *read* " E. PFLÜGER."
395 | 19 ,, " this vol., ii, 395 " *read* " this vol., ii, 404."

* From bottom.